THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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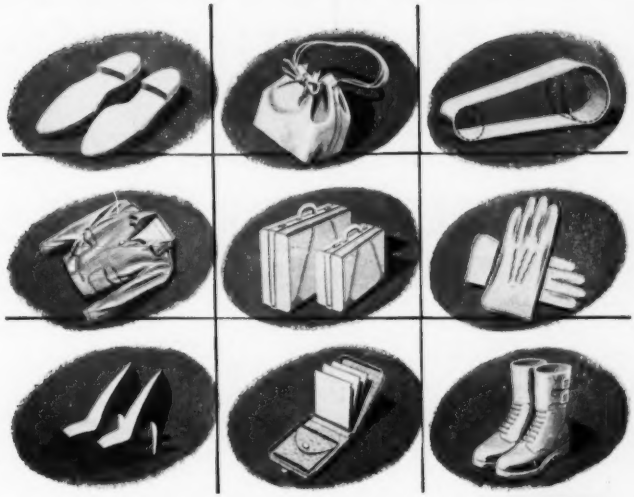

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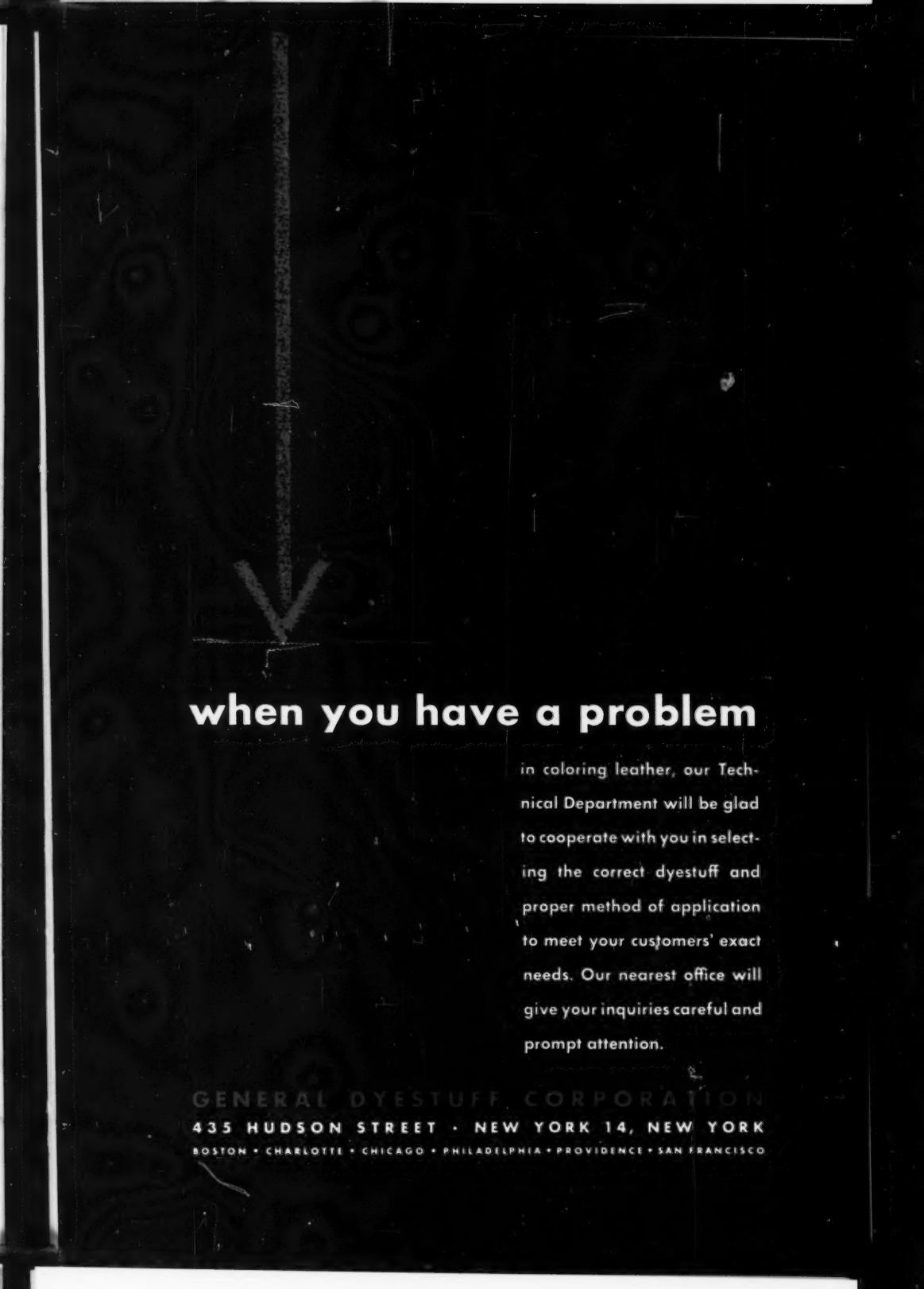
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in coloring leather, our Technical Department will be glad to cooperate with you in selecting the correct dyestuff and proper method of application to meet your customers' exact needs. Our nearest office will give your inquiries careful and prompt attention.
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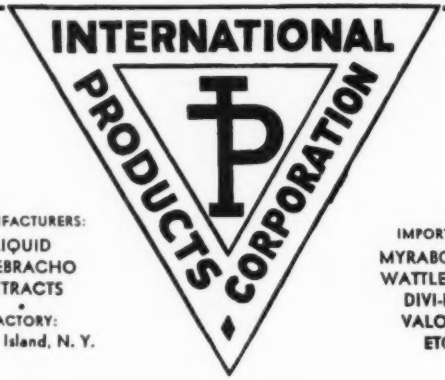

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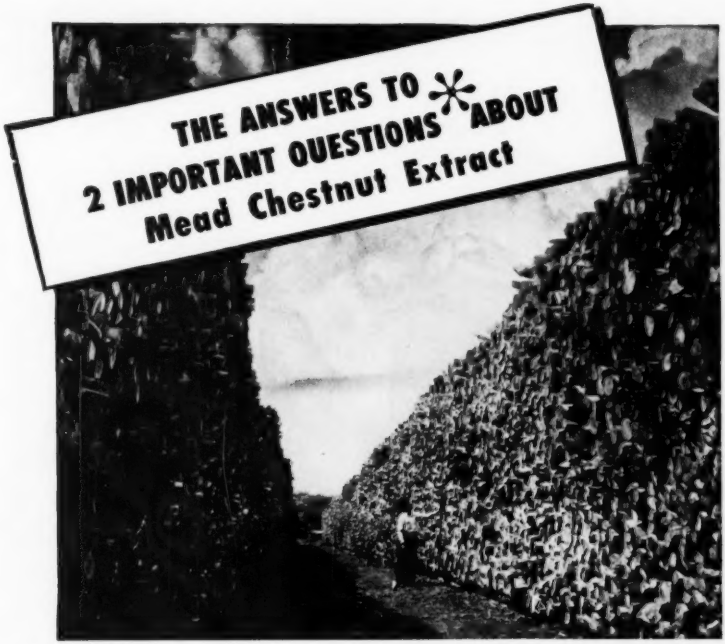

This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

MEAD CHESTNUT EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia

Good looks on handbags of any price

Good value from any Du Pont dye

These two handbags could represent an extreme range in leather costs. But it is the quality of the dye—not the grade of the leather—that determines their color performance. Each was dyed with a deep-penetrating red, and each has full, bloomy undertones.

Both bags will perform well as to color because each was processed with a Du Pont Dye—a level-dyeing, uniform dye that has complete compatibility with syntans. Du Pont's technical-service experts helped the manufacturer in maintaining or even upgrading the leather quality in dyeing.

In Du Pont's line of dyes, there's a wide range of colors and shades in colors—a dye for any leather you process. For technical-service helps, write E. I. du Pont de Nemours & Co., (Inc.), Dyes and Chemicals Division, Wilmington 98, Delaware.

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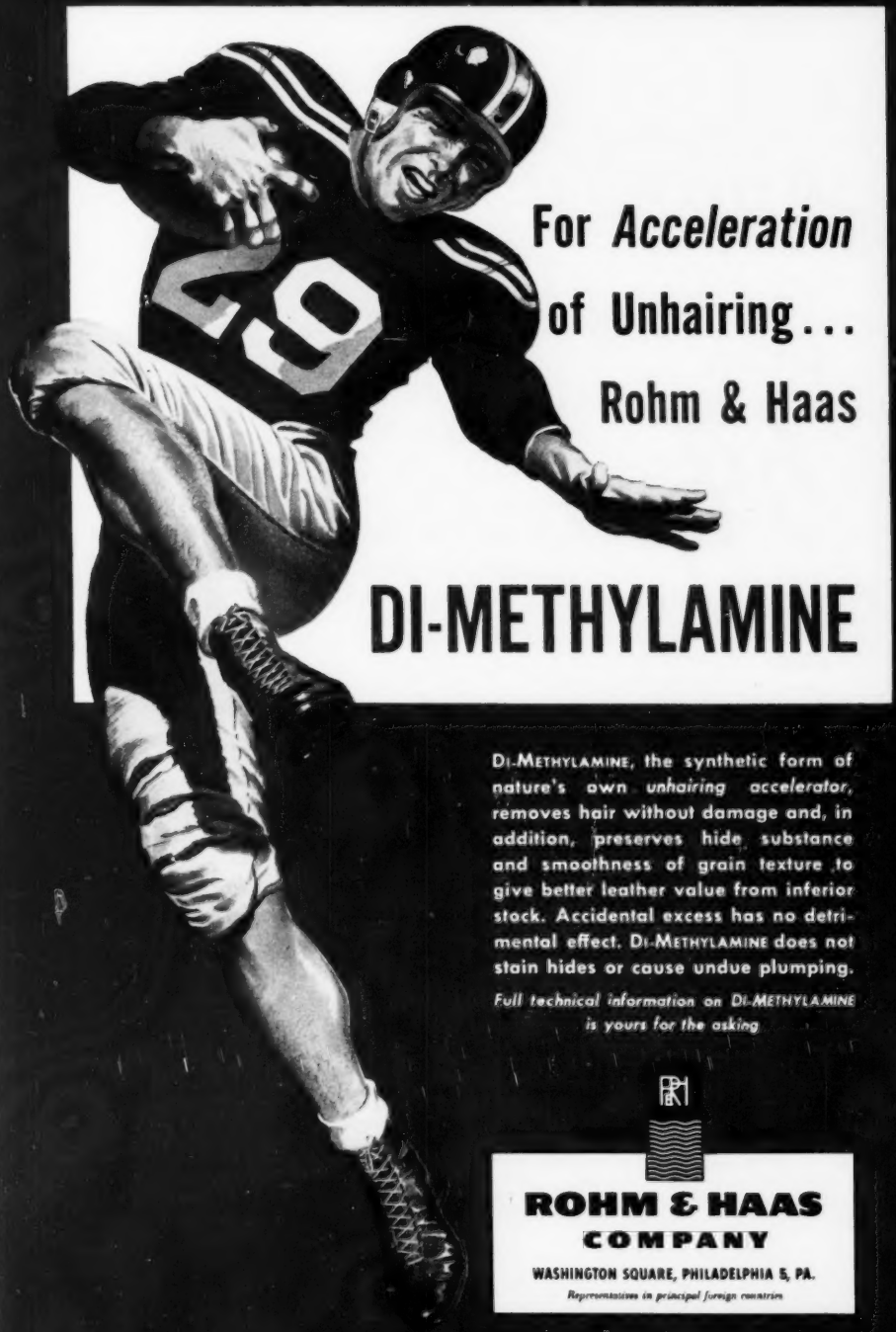

For *Acceleration* of Unhairing... Rohm & Haas

DI-METHYLAMINE

DI-METHYLAMINE, the synthetic form of nature's own *unhairing accelerator*, removes hair without damage and, in addition, preserves hide substance and smoothness of grain texture to give better leather value from inferior stock. Accidental excess has no detrimental effect. DI-METHYLAMINE does not stain hides or cause undue plumping.

Full technical information on DI-METHYLAMINE is yours for the asking

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ATLAS *Refinery, Inc.*

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What Hooker Sodium Sulfhydrate does for the Leather you make...

SOLE LEATHER—With Hooker Sodium Sulfhydrate, you can increase sulfide strength of the unhairing solution just as desired, and still keep alkalinity low. This means easy unhairing in limited time. Hides are ready when desired—without loss of hide substance from long immersion. *Results:* a minimum of swelling . . . greater yield of tight, solid, smooth-grained leather . . . a significant saving of time and extra operations in the beam-house.

CALFSKINS AND HORSEHIDES—The tender grain of these skins is protected by Hooker Sodium Sulfhydrate from excessive swelling and plumping caused by high alkalinity. With Sodium Sulfhydrate, a minimum of swelling takes place, resulting in a better yield of fine, smooth leather.

GOATSKINS—Destructive bacterial action is held to a minimum, because Hooker Sodium Sulfhydrate increases the solubility of the lime and permits more constant pH value than with Sodium Sulfide. Sulfide content can be built up, with low alkalinity. Alkalinity can be increased or held as desired, without affecting sulfidity. *Result:* Greatly simplified control of quality, even with skins that vary widely in sensitivity.

When dissolved in lime, Hooker Sodium Sulfhydrate forms only half as much caustic soda as the same quantity of Sodium Sulfide forms. This gives you precision control of unhairing solutions—and many other advantages. Write today for a copy of Hooker Bulletin 500, "Sodium Sulfhydrate for the Leather Industry," which suggests unhairing procedures for various leathers.

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level dyeing,
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specify

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Nigrosines

Versatile and highly adaptable to many phases of leather dyeing, Calco's NIGROSINE WSB #50 and NIGROSINE WSJ #78 give excellent results on vegetable and chrome tannages. They work well in dyeing by drum or brush and in finishing formulas.

The Calco NIGROSINES are available in crystal or powder form, ranging in shade from blue to jet.

Your Calco representative will gladly give you full information on these and the many other specialized dyes in the Calco line.

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The power unit, which is enclosed in metal housing 16½ x 15 x 9¾ inches high, consists of 1/6 h.p. direct current motor, a dry disc rectifier to convert a.c. to d.c., and a rheostat with knob and dial on front of the housing for varying the speed between 70 and 300 oscillations per minute with load, with horizontal stroke of 1½ inches. Power consumption 200 watts.

The box-type carrier is of anodized aluminum 18 x 12 x 3¾ inches deep, with rubber covered floor, and slotted sides and ends to take adjustable, rubber covered bars lengthwise and crosswise for holding various sizes and types of bottles and flasks in position. The utility of the Shaker is increased by the use of the ½-inch corner posts on which a variety of clamps and glassware can be mounted for shaking.

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JOURNAL OF THE
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VOL. XLVII DECEMBER 1952 No. 12

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SECRETARY'S NOTICE

Nitrogen Determination

At the 1952 Annual Meeting the recommendation of the committee on Hide Substance Determination to the effect that the method published by Dahl be accepted as a provisional method was reported. The committee published their findings in the January 1952 issue of our Journal.

It was by motion, duly moved and carried that the recommendation of the committee be accepted and that the method of Dahl et. al. becomes a provisional method of the Association.

Nominating Committee – 1953

The retiring president, Dr. Koppenhoefer, in keeping with a provision in the by-laws has appointed the following nominating committee for 1953.

A. G. Fleish of Pfister and Vogel Tanning Company

C. David Wilson of Rueping Leather Company

Robert S. Adams of Eisendrath Tanning Company, *Chairman.*

Tellers for the 1952 *Election*

Messrs Roll, Stumpf and Compton were appointed tellers to count the 1952 election results.

BUREAU OF EMPLOYMENT

Wanted: Instructor with good theoretical background in chemistry or biology. Recent graduate with some practical experience in the leather industry preferred. The conditions are pleasant and the opportunties for advancement are governed entirely by the individual. Please send complete resume and references to Dr. Albert E. Chouinard, Head, Department of Leather Engineering, Lowell Textile Institute, 1 Textile Ave., Lowell, Massachusetts.

Notes on the Crocking of Suede Leather*

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Technical Laboratory
E. I. du Pont de Nemours & Co., Inc.

Introduction

Suede is the French word for Sweden. The term as applied to leather is said to have had its origin when early Scandinavian invaders were observed to wear garments made of rough leather with the flesh side out. There have been many advances in leather from the battle dress of those early invading warriors to the modern suede which plays such an important part in today's

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wardrobe. One of the major improvements is the wide range of beautiful colors in which the present-day product is available.

Suede leather intended for shoes, gloves and garments may be colored to almost any shade dictated by personal taste or the varying requirements of styling. However, during consumer usage a frequently experienced disadvantage of articles made of suede leather is their tendency to crock, or transfer colored matter to the hand or clothing.

General Remarks

Consideration of the crocking phenomenon indicates that colored matter transferred from suede leather may be due to one or more of the following causes:

1. Unfixed water-soluble dyestuff.
2. Mechanically held pigmented dyestuff.
3. Loose colored leather fiber or buffing dust mechanically held on and between fibers which comprise the nap.
4. Dyed particles of clay or flour used for "pearling."

Since factors (1) and (2) involve dyeing, due consideration must be given to the selection of dyes best suited to the shade desired, to the dyeing characteristics of the leather and to attainment of optimum conditions with respect to processing variables. Among the more common causes of crocking associated with dyes and dyeing are:

(a) Incomplete fixation and mechanical retention of dyes due to inadequate wetting of the pearled or crusted leather prior to dyeing.

(b) Use of dyes unsuited to coloring suede leather in deep shades and dyes having low exhausting capacity on the leather.

(c) Concurrent application of anionic (acid, direct) and cationic (basic) dyes or use of anionic dyes followed by cationic dyes with insufficient rinsing between additions.

(d) Process maladjustments, principally with regard to dyeing time and pH level, temperature and concentration of the dyebath.

(e) Use of filling materials which resist dyeing.

Inasmuch as both dyeing characteristics of suede leather and shades desired vary over wide ranges, it is impossible to lay down precise rules to govern all cases. However, with regard to the effect of dyebath concentration on crocking, experience in the laboratory, confirmed by numerous full scale drum runs, indicates that concentrations of dyes within the range of 1.0 - 2.0 per cent appear to be optimum for minimizing crocking of medium-to-heavy shades.

Factors (3) and (4) in the foregoing list may be considered "mechanical" in nature since they comprise retention on and between the nap fibers of particles of loose colored matter which originate either as added filling material or as leather fiber abraded by the mechanical buffing operation.

Recent studies at the Technical Laboratory indicate that loose particles of matter embedded within the nap before or after dyeing are largely responsible for the crocking of suede leather dyed under optimum conditions.

Experimental

Microscopic Examination

Transferable particles removed from undyed, pearl-buffed chrome-tanned goatskin suede and dark brown, top buffed goatskin suede of equivalent tannage were examined by means of the electron microscope. Acid and chrome dyes were used for coloring the brown suede. The dusts were flushed from the suede with xylene solvent and deposited from the solvent on the microscope screen for visual and photographic examination. Photomicrographs (Magnification: 3,200 X) revealed, in both cases, irregularly shaped particles varying in size from about one micron to over twelve microns. There appeared to be no significant differences in the sizes and shapes of particles removed from the colored and the uncolored leather (Fig. 1). The marked similarity of the colored and uncolored particles revealed by the microscope offered striking evidence that the cause of crocking of the dyed suede was inherent in the pearled suede before dyeing.

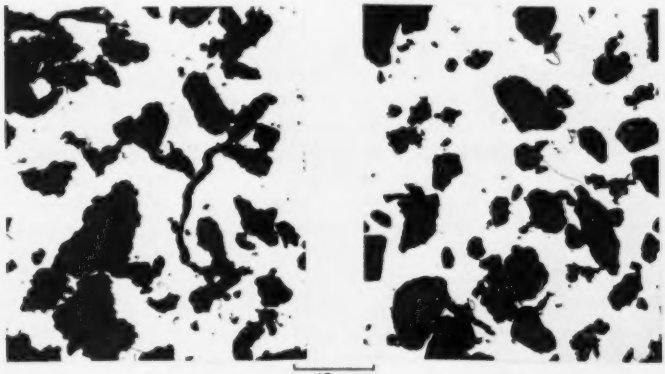

FIGURE 1
PARTICLES REMOVED FROM SUEDE LEATHER
(a) FROM UNDYED PEARL BUFFED SUEDE
(b) FROM DARK BROWN SUEDE DYED WITH ACID AND CHROME DYES.

Effect of Pearl Buffing

Buffed and unbuffed goatskin chrome tanned for suede was dyed for 30 minutes at 130°F. with 7.5 per cent (on dry weight) of a blue-black acid dye

(Colour Index No. 246). The dyebath ratio in both cases was 5:1. Four per cent of formic acid (87%) was used to exhaust the dyebaths, followed by rinsing and fatliquoring with 1.0 per cent of sulfated animal/fish oil. After drying the leather was staked lightly. Pieces of each leather were then tested for crocking.

Dry crocking was evaluated by the A.A.T.C.C. Standard Test Method 8-45: Colorfastness to Rubbing (Crocking) [1]. By this method the leather under examination was given 20 rubbings with white cotton cloth mounted over a wooden finger in a machine having a rubbing motion and weight simulating the action of a human finger and forearm. The degree of crocking was measured by the amount of color transferred from the specimen to the cloth when compared with color chips in the A.A.T.C.C. Color Transference Evaluation Chart. The degree of crocking was expressed by numbers in a five membered scale wherein 1 represented the poorest crockfastness and 5 indicated essentially no color transfer. Using this test the dyed unbuffed leather yielded a 4–5 crockfastness rating, whereas the dyed pearl buffed leather rated 1. Figure 2 shows the relative amounts of color transferred. These results offered additional evidence that crocking was caused largely by fibrous debris abraded by the pearl buffing operation and deposited on and between the fibers prior to dyeing.

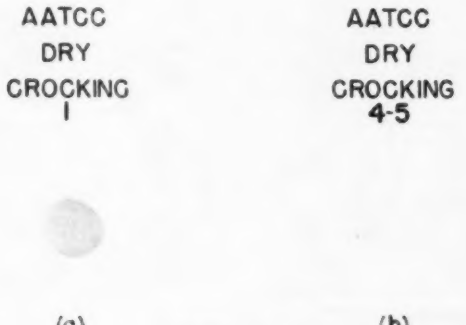

FIGURE 2

CROCKFASTESS OF DYED GOATSKIN CHROME TANNED FOR SUEDE

(a) PEARL BUFFED PRIOR TO DYEING

(b) NOT BUFFED PRIOR TO DYEING

Test pieces of unbuffed and buffed pearled goatskin chrome tanned for suede were dyed with several other widely used leather colors by the aforementioned procedure and tested by the A.A.T.C.C. Standard Test Method 8–45. The results are shown in Table I.

TABLE I

Results of Dry Crocking Tests

Dyestuff			A. A. T. C. C. Crockfastness Rating*	
Per Cent Used	Description	Color Index No.	Unbuffed Leather	Pearl Buffed Leather
18	Direct Blue	401	4–3	2–1
10	Direct Blue	—	3	2
10	Acid Blue Black	246	4–3	1
10	Direct Black	—	3	1
10	Acid Green	666	4–3	1
12	Chrome Brown	105	4–3	1
12	Acid Brown	235	4–3	1
10	Acid Red	176	3	1

*1 indicates poorest crockfastness, 5 indicates virtually no crocking.

Effect of Top Buffing

As previously shown, unbuffed goatskin chrome tanned for suede and dyed with 7.5 per cent of acid blue black dye (C. I. #246) exhibited an A.A.T.C.C. crockfastness rating of 5-4. After top buffing with No. 5/0 paper, followed by thorough brushing to remove free surface dust a rating of 2 was obtained. Thus, serious lowering of dry crockfastness due to top buffing was indicated. Comparable degradation of crockfastness was observed when dyed wool serge was subjected to light buffing with fine-grained buffing paper. Scoured wool serge was dyed at the boil with 5.0 per cent of the blue black acid dye (C. I. #246) employed in the preceding experiment with leather. Testing revealed a crockfastness rating of 3. This material was buffed lightly with No. 8/0 paper and again tested for dry crockfastness. A rating of 1 was obtained. Repeated brushings with a stiff bristled brush failed to remove enough embedded particles to improve the poor crockfastness. Figure 3 shows the relative amounts of color transferred.

This experiment was repeated, with similar results, using 5.0 per cent of a black chrome dye (C. I. #299) applied at the boil and top chromed. In this instance ratings were 2 before buffing and 1 after buffing. These results on wool serge confirmed the earlier findings of Millson, et al.[2] who reported that well-dyed, crock-free wool fabrics often crock excessively after being subjected to the mechanical shearing operation frequently used for finishing. This is not due to the dye or dyeing procedure but to the presence of colored wool dust arising from shearing.

TABLE II

Crockfastness of Leather and Textile Materials

Material Tested	A. A. T. C. C. Dry Crocking*: Before Buffing	After Buffing
Suede leather dyed with 7.5% of C. I. No. 246 (Pearl buffed prior to dyeing)	1	1
Suede leather dyed with 7.5% of C. I. No. 246 (not pearl buffed)	5–4	2
Wool serge dyed with 5.0% of C. I. No. 246 (acid dye)	3	1
Wool serge dyed with 5.0% of C. I. No. 299 (top chromed)	2	1
Vat dyed cotton corduroy (medium blue shade)	5	3
Vat dyed cotton drill (medium blue shade)	4	3–2
Vat dyed cotton twill (olive drab shade)	5–4	3
Vat dyed cotton sateen (olive drab shade)	5–4	3

*1 indicates poorest crockfastness, 5 indicates virtually no crocking.

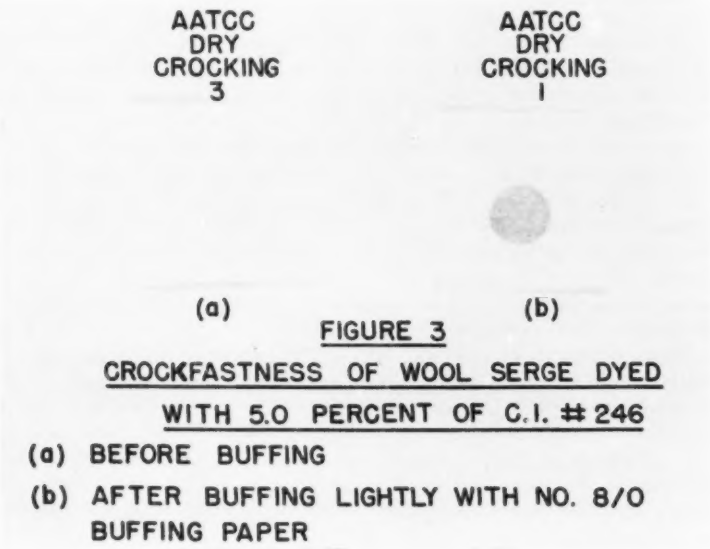

FIGURE 3

CROCKFASTNESS OF WOOL SERGE DYED WITH 5.0 PERCENT OF C.I. # 246

(a) BEFORE BUFFING

(b) AFTER BUFFING LIGHTLY WITH NO. 8/0 BUFFING PAPER

Dry crockfastness tests of textile materials before and after buffing were extended to cover a variety of cotton fabrics dyed with vat colors. Results are shown in Table II. Inasmuch as vat dyes are believed to be irreversibly fixed by a strong union with cellulosic material [3], the lowering of crockfastness by buffing appeared to be due to colored dust abraded by the mechanical operation rather than to unfixed dyestuff.

The foregoing experiments indicated that colored fiber dust abraded by the buffing operation and embedded on and between the fibers contributed largely to crocking.

Summary and Conclusions

Crocking measurements of both buffed and unbuffed goatskin chrome tanned for suede and dyed under equivalent conditions are described and discussed. Comparative evaluations of the crockfastness of suede leather and wool serge colored with the same dye are described. Data obtained indicate that the crocking of suede leather dyed under optimum conditions may be attributed largely to particles of colored leather abraded by the buffing operation and embedded within the nap of the leather. These particles (ranging in size from about one micron to over 12 microns) may have their origin both before dyeing (during "pearl buffing") and after dyeing (during "top buffing").

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Snythetic Fat Replacement Materials for Leather

V. Selection of Specific Exchange Fats for Study and Synthesis. Objectives of the Synthetic Program. The Synthesis and and Properties of Analogues of Derminolnarben Oil and Chlorinated Waxes.*

By Esther Liggett, Betty M. Orians, Lois Barr, William Zimmer and J. B. Brown

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In previous reports [1], [2] we have listed a large series of exchange fats for leather which had been proposed by the Germans during the period of war-

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time shortages of natural fats and oils for replacing the natural fats in leather technoiogy. Of these numerous exchange fats only about one-half dozen of them manufactured by I. G. Farbenindustrie were selected by us for study and duplication in this work. These were selected for several reasons. First, while specific information as to chemical composition for most of the materials was meager, we had available from the production sheets of the Schultz-Schubert report [3] details of composition and manufacture of several I. G. Farben products. In the second place, we had available authentic specimens of the following materials: Derminolnarben oil; Derminollicker 1, Derminol oils 1 and 2 and Immergan. Thus, we could study these products first hand, and they could be screened on a small scale in leather at the Tanners' Council Laboratory in Cincinnati. During the progress of our investigation other authentic materials were furnished us, including Densodrins NR and NW, Weichharz XF, Derminol fat 2A, Diesel oil (Kogasin II), Derminol IH and Chloro-Kogasin. The third reason for selecting the materials we did is the inference that by the end of the war the products in question were actually in use as exchange fats in amounts sufficient to meet most of the German requirements. Production claimed for 1943 [4] was as follows:

Exchange Fat	Metric Tons per annum
Derminol B	63
Derminol L	34
Derminol Fats 1 and 2	539
Derminollicker 1	1619
Derminolnarben oil	217
Leather Oil Hö 1/90	3340
Derminol Oil 1	3165
Derminol Oil 2	511
Densodrin NH	106
Densodrin W	3
Total	9597

The following is an estimate of the annual German needs of fat materials for leather [5]:

Product	Approximate Need Metric Tons
Train (fish) oil	5000
Beef Tallow	2500
Other fats and oils	2500
Mineral Oil	1800
Total	11,800

For the preceding reasons our program of synthesis was therefore confined mainly to the synthesis of analogues of Derminolnarben oil, Derminol fats 1 and 2, Derminol oils 1 and 2 and Derminollicker 1. Special attention was devoted to Immergan, because of its possibilities as an oil-tan of easy manufacture and of its unique properties. Our early work in this direction was described in No. 1 of the present series of papers [6]. Our decision to restrict our work to the above fat substitutes was strengthened from time to time by the results of the screening program at Cincinnati [6, 7] where it was shown that the materials in question are effective replacements for the natural fats in leather manufacture.

(a) Objectives of the Synthetic Program

The experimental part of our work was directed to three main objectives, namely, (a) chemical examination of authentic specimens of exchange fats which were at our disposal; (b) synthesis of materials as nearly like the replacement materials of the Germans as possible; and (c) synthesis of materials, basically like those of the Germans, but from raw materials, which are commercially available in the U. S. and which would be likely to be available in wartime.

It was clear from the start that most of the Germans exchange fats were derived more or less fortuitously from chemicals which were produced primarily for other purposes. Thus, the basic raw material for most of these replacement fats was Kogasin, a synthetic crude oil made by hydrogenation of water gas, and thus derived from coal. The kerosenic fraction of this synthetic oil was used mainly as a motor fuel, (Diesel oil) but it was also applied to the synthesis of detergents, food fats, and numerous other uses. Diesel oil, when chlorinated to 40 per cent of chlorine, gave an oil which could be used as a leather oiling agent and was a principal ingredient of Derminol oil 1, Derminollicker 1 and Derminol fat 2. Very early in our work, therefore, we explored the synthesis of Derminolnarben oil and were confronted with the problem of finding available a hydrocarbon mixture similar to Kogasin II which was a mixture mainly of straight chain C_{18-20} paraffinic hydrocarbons. No such mixture was found in this country. We were informed that Pennsylvania crude oil yielded a fraction similar to Kogasin II, but found upon further investigation that the isoparaffins, naphthenes and aromatics of Penn crude oil precluded its use in preparing chlorinated derivatives, because of their instability. During the course of our work, two products, composed almost entirely of straight chain paraffins, have become available, namely, Ultrax 20 (Atlantic Refining Co.) and C_{12-20} hydrocarbons (Shell Oil Co.). Both of these yield highly stable chlorine derivatives.

As the program of synthesis developed, we lost sight almost entirely of the objective of merely matching the German products, but rather endeavored to synthesize analogues which were designed to be superior to the German products.

(b) Acknowledgment of Cooperation from American Industry

From the very beginning of this project, we were given invaluable assistance by American chemical industries and especially by individuals in these industries, who contributed their know-all of the problems at hand and who were responsible for supplying us valuable raw materials for our program of synthesis. Space does not permit making due acknowledgment of all of this assistance, but the more outstanding of these contributions are briefly noted here. We wish to acknowledge their invaluable contribution to our work. Dr. J. H. Crowell, of the U. S. Bureau of Mines at Pittsburgh, made available a supply of Fischer-Tropsch Diesel oil, secured by the Navy from the Harnes Co. in France. From this material we were able to prepare Derminolnarben oil which was practically identical with authentic material we received from Germany. Some of this Diesel oil was also converted to sulfonyl chlorides.

The duPont Company (Drs. S. R. Dietrick, H. W. Bradley, G. H. Patterson, W. H. Lockwood, A. A. Pavlic, and others), Wilmington, Del., supplied us with specimens of alkyl sulfonates, a wide series of fully and partly sulfochlorinated hydrocarbons (Immergan analogues) and some special chlorinated polythenes. Many of these materials were made by them *to our specifications*. Our investigations have been responsible in part for the interest of this company in developing some of these materials as tanning agents.

The Hercules Powder Co., of Wilmington, Delaware, and Parlin, N. J., (J. B. Martin, W. T. Kiessling, A. B. Olsen, and others) gave valuable assistance by preparing chlorinated hydrocarbons and waxes and furnished us with specimens of their Chlorafins, as well as a series of Chlorafins of lower chlorine content, made especially to order. They also chlorinated Crown Wax and Ultrax 20 wax for our intermediate and large scale testing program.

Our contacts with General Aniline and Film Corp., New York City, were made through Dr. P. G. Stevens. Others of the staff of this company to whom we are indebted are Drs. F. M. Meigs, A. O. Zoss, and C. E. Schildknecht. Drs. H. M. Shine and P. M. Kirk assisted especially in the commercial angles of the problem. This company is particularly interested in the program from the point of view of practical applications of polyvinyl ethers, Emulphor STH, Acid H and Amide H, and possibly Derminol oil 2. They furnished us special preparations of all of these except the last, including intermediate scale batches of Emulphor STH and Igevin J-30. They have prepared the Igevin of k-value 22 for the large scale tests now being made.

Socony-Vacuum Laboratories (Brooklyn), through Dr. R. M. Koppenhoefer, prepared several special hydrocarbon fractions for us.

Two divisions of Union Carbide and Carbon Corporation gave us noteworthy assistance. Carbide and Carbon Chemicals Corp., Cleveland, through D. S. Alcorn and J. B. Harlow, furnished us with specimens of phenoxypropylene oxide and Stabilizer C–2, and specimens of a considerable series of

alcohols, for use in Derminol oil 2 synthesis. The Halowax Products Division (N. Y. City, A. E. Irvine, Mr. Krummel), worked with us along the line of their interest in chlorinated hydrocarbons and xylene-formaldehyde resins. Also, they supplied us with two specimens of Derminol oil 2, made according to our specifications.

The Nopco Chemical Co., Harrison, N. J., through Mr. C. E. Retsch and Dr. Frank J. Sprules, supplied us with specimens of alkyl benzenes for synthesis of Derminolnarben oil and analogues.

The Chemical Products Department of Standard Oil of Indiana (H. R. Peterson) supplied us with certain Indoil sulfonates. Drs. J. K. Roberts and T. H. Rogers prepared a special gas oil fraction from Synthol (American Fischer-Tropsch) for a Derminolnarben oil synthesis.

Dr. H. B. Tucker of the Procter and Gamble Co., Ivorydale, O., sent us several gallons of C_{8-10} alcohols for Derminol oil 2 synthesis. O-,m-, and p-xylene specimens were sent us by the Oronite Co., also several special ronite sulfonates. We are indebted to the Sonneborn Sons, Inc., Chicago, for several specimens of sulfonates; to the Atlantic Refining Co. (Drs. Neidig and Hersberger), Philadelphia, for important contributions of Ultrax 20; to the Shell Oil Co. for several paraffinic hydrocarbon fractions; to the Kendall Oil Co. for several of the Kensols.

(c) Examination of Derminolnarben Oil

Derminolnarben oil, or Chlorokogasin, was alleged to be a mixture of chlorinated hydrocarbons of C_{10-20} series, and to contain 40 per cent chlorine. The material in question, obtained in Germany by the Schultz-Schubert team*, was a reddish brown oil of about the viscosity of neatsfoot oil. It gave off a strong odor of HCl gas. Analytical data were:

Iodine no.	0.3
Chlorine, per cent	38.8
Fat no.	97.7
Saybolt viscosity at 54.4°, 90.2–95.3 S.U.S.*	

*Hereafter, all temperatures are in °C, unless otherwise indicated.

Practically all material came over when distilled at 5 mm. pressure. (See Table I) The following fractions were obtained:

TABLE I

Results of Distillation of Derminolnarben Oil

Fraction No.	B. P. °C. 5mm.	Wt. g.	Per Cent Chlorine
I	up to 162	8.2	34.5
II	162–203	30.6	39.0
III	203–220	26.0	41.2
IV	220–235	18.7	39.6
Residue		7.0	——
Trap		1.6	——
Amt. distilled		99.3	
Total recovered		92.1	

It is clear from the chlorine analyses in Table I that appreciable decomposition with loss of HCl occurred during distillation.

(d) Synthesis of Chlorinated Hydrocarbons (Derminolnarben Oil Analogues) and Waxes

(1) *The Problem*

Derminolnarben Oil (subsequently referred to as DNO) was a leather oil, made by chlorinating Kogasin II to a chlorine content of 40 per cent [2]. Its penetrating qualities into leather were excellent, but it possessed the disadvantage of poor water-repellency. However, by the addition of such materials as chlorinated wax (Derminol fat 2) and Igevin (Derminol oil 1) an exchange fat of satisfactory water repellency could be made. The raw materials for manufacture of DNO were Kogasin II and chlorine; hence, DNO was inexpensive and competitive with natural fats from this point of view.

The synthesis of DNO exactly like the German product, at present, or in the near future, is practically out of the question, since a raw material identical with Kogasin II is not available in this country. We were informed that experimental Fischer-Tropsch synthesis in the U. S. is not directed towards making a product like the German Kogasin. Furthermore, crude oil fractions from American petroleum are quite unlike Kogasin II in that they invariably contain important amounts of naphthenes, aromatics and branched chain hydrocarbons, all of which, when chlorinated, give products too unstable for the purpose. The problem is further complicated by the question of stability of chlorinated hydrocarbons in general. Attempts to prepare materials of this type as fireproofing agents have usually resulted in materials which liberate HCl on standing [9]. Thus there is considerable prejudice in this country against these materials. Therefore, the questions of available raw materials, of stability of products, and of stabilizers are important ones. It was only after considerable work on this project that hydrocarbon fractions became available which gave products of satisfactory stability, in fact, more stable than German DNO.

During the course of our experimental work it was necessary for us to prepare certain chlorinated waxes: these may be considered as analogues, of Derminol fat 1, a chlorinated hard wax containing 12 per cent chlorine, or simply as novel products. Because the problem of synthesis of chlorinated waxes is practically identical with that of making DNO analogues, our wax chlorinations are described in this section. However, no actual formulations into Derminol fat 2 analogues will be described at this time.

(2) *Description of Raw Materials for Synthesis of Derminolnarben Oil Analogues and Chlorinated Waxes.*

Within a few weeks after this project was started we were fortunate to secure from the Bureau of Mines a specimen of Fischer-Tropsch Diesel oil,

made in Harnes, France. Its boiling point range, 195–328°, was very close to that alleged for Kogasin II. Dr. Crowell reported the following analytical data:

Bromine no.	8.0
Olefins	8.6%
Aromatics	0
Wax	0
Sp. g.	0.765 at 20°
Viscosity	3.13 centistokes at 20°

As the work progressed, we were supplied with numerous other petroleum fractions and waxes through the cooperation of individuals and the companies with whom they were associated. Some of these were especially prepared for us; others were products commercially available or being developed. Important analytical data and compositions follow:

Heavy Alkylate and Penn Crude Fraction (PCF). Socony-Vacuum Oil Company.

Heavy alkylate was a highly branched chain hydrocarbon fraction, while PCF was a specific boiling range cut from Penn crude oil. These gave the following data, which were furnished us by Dr. R. M. Koppenhoefer:

	Heavy Alkylate	PCF
Gravity API	44.2	41.6
Sp. g.	0.8054	0.8174
Pour	Below O	Below 0
Carbon-hydrogan ratio	5.94	6.22
Diesel index	85.2	71
Distillation range	221–299°	221–315°

Synthol Gas Oil.

This fraction was cut from a pilot scale batch of American Fischer-Tropsch crude oil of the approximate boiling range of Kogasin II; it contained approximately 14 per cent aromatics, no naphthenes. Olefins were roughly half straight chain and half branched chain, the double bonds being distributed throughout the molecule. The iodine number of this material was 98.7.

Hydrogenated Fish Oil.

A specimen of fish oil was hydrogenated for us by the Procter and Gamble Co. to an iodine number of 3.4.

Kensol Fractions.

The Kendall Refining Co. supplied us with 5 gal. each of Kensol 16 and Kendall C_{22-24} fraction. The former is a stock preparation with them, the latter a special fraction which was being studied for future development. The Kensol 16, is mainly a C_{17} fraction with appreciable amounts of naph-

thenes and aromatics. Its boiling range was 572–590° F.; iodine number 6.5 (ASTM '42); viscosity 45.3 S.U.S., 77° F. In addition to the lots sent us, specimens of both of the above fractions were especially treated to remove non-paraffinic material and supplied to the duPont Co. for conversion into sulfonyl chlorides.

Kensol 31 was a special fraction, boiling 467–495° F., and consisting of about ½ paraffins and ½ naphthenes.

Nopco Hydrocarbon.

This material, furnished by Nopco Chemical Co., is an alkyl benzene with C_{12-14} side chain, probably branched.

Dodecane; Hexadecene; Hexadecane.

Pure hydrocarbons, purchased from the Connecticut Hard Rubber Company.

Ultrax 20.

A nearly pure, paraffinic hydrocarbon melting at 35°. This was in pilot scale production by the Atlantic Refining Co. in 1948. It is composed mainly of C_{18-20} paraffins. Sp. g., 0.7967; iodine no., 0.24; BP., 360–400°F.

Shell Hydrocarbons

Four new hydrocarbon preparations by Shell Chemical Corp. became available, when experimental work on this project was nearly completed. One of these, C_{12-20}, was very similar to Kogasin II in boiling point range. It was alleged to be over 95 per cent normal paraffins of C_{11-21} carbon content. The other three Shell preparations were: C_{12-14}; C_{15-17}; and C_{18-20}. The last of these was apparently similar to Ultrax 20.

Crown Wax 700 (*Petrolite Co.*)

M. P. (ASTM)	92° minimum
Carbon	84.3%
Hydrogen	15.2%
Sulfur	0.36%
n^{100}	1.4395
Mol. Wt.	574 ($C_{41}H_{84}$)

Crown Wax 1010 (*Petrolite Co.*)

M. P. (ASTM)	195–200°F.
Acid No.	0
Sap. No.	0

Crown Wax 1035 (*Petrolite Co.*)

M. P. (ASTM 192-200° F. Indiana)

Superla Wax (*S. O. of Indiana*)

M. P. (ASTM)	167.2°F.
Sp. g. 60/60	0.942
Mol. Wt.	587
n^{84}	1.446

Amorwax 1200*A* (*Pennotex Oil Co.*)

M. P.	87–93°

Practically identical with Crown Wax 700, except slightly more color and containing more low melting material.

(3) *Method of Chlorinating Hydrocarbons and Waxes.*

The German method of chlorinating Kogasin II [3, 10] was simply to pass chlorine through the hydrocarbon in lead lined vessels at a temperature of 90–100°. Our laboratory was not equipped to perform such an operation and our early chlorinations were carried out with rather crude apparatus in a hood with a 60 w. lamp as the sole catalyst. We later developed a procedure which was adapted to use in the open laboratory. For amounts of hydrocarbon up to 1600 cc. we used an all-glass chlorinating cylinder, 75 cm. high and 10 cm. in diameter, which was fitted with a male stopper through which an 8 mm. glass tube conducted chlorine gas to the bottom of the cylinder. The chlorine was dispersed into fine bubbles through a sintered glass bubbler. A glass side arm, located at the top of the cylinder, just below the stopper, conducted waste gases out of the apparatus, most of the HCl and residual chlorine being retained by passing the gases through a 5-liter flask containing alkali. The charge was heated by 2 infra-red lamps, the temperature being maintained by adjusting these lamps to a proper distance. At the start of each chlorination there was usually a 20-30 minute lag phase to the reaction. Chlorine was at first absorbed slowly, usually with considerable darkening of the charge. Then, rather suddenly, fine bubbles of HCl began to appear, the color rapidly bleaching. When chlorine introduction was interrupted for any reason, the color often reappeared on standing. As soon as HCl evolution began, the rate of chlorine addition could be increased. Generally speaking, the reaction tended to slow up when the chlorine content reached 40 per cent. Also, it was found that chlorination of waxes was generally more difficult, higher temperatures being required.

We were told by those experienced in commercial chlorinations that stirring and other methods assuring rapid mixing of the chlorine with the charge might affect the composition of the product. Experiments to inquire into this factor gave no positive information which verified this statement.

For charges larger than 1600 cc., we used standard Pyrex Cylinders, 6″ x 12″ and 6″ x 18″. The former would take up to 4 liters and the latter 7 liter of charge. These cylinders were fitted with a composition cap, grooved closely to fit the top of the cylinder. Holes were placed in this cap for glass tubes to introduce the chlorine and carry away the gases and for a thermometer. A rubber band was employed to make the apparatus gas-tight.

The course of chlorinations was followed by increase in weight, by hydrometer (sp. gr.) and by chlorine analysis. When any considerable series of products was to be made from a single raw material, as for example Ultrax 20, we found it most convenient to run a progressive chlorination of the material, taking out specimens from time to time and determining the refractive index and chlorine content. In subsequent chlorinations the refrac-

tive index could be used as a criterion of the progress of chlorination. The final criterion of any given product was, of course, the chlorine content, which was determined by Volhard titration following fusion in the Parr peroxide bomb.

When the chlorine content of a given product was approximately what was desired, air was passed through the charge for 2–4 hours to remove most of the excess HCl. The product was then removed to a glass vessel of suitable size, and stirred hot with powdered potassium carbonate. It was then filtered and analyzed. The removal of the last traces of HCl was very difficult, so that each product had an appreciable acid number. Upon standing in closed glass vessels most of the products developed a strong odor of HCl, caused by slow liberation of HCl. The actual amount of HCl formed, however, was relatively insignificant. The question of stabilizers and tests of stability are discussed later.

(4) *Description of Batch Chlorinations of Hydrocarbons and Waxes.*

In Tables II and III which follow are to be found the data on a large series of chlorinations of hydrocarbons and waxes.

Only those products in Table II which are made from Diesel oil and from Shell C_{12-20} hydrocarbons are close analogues of DNO. The products obtained from heavy alkylate, Nopco [4], and hydrogenated fish oil and Kensol 16 were decidedly more viscous than DNO. The comparative stabilities of many of these preparations are described later.

Chlorination of the waxes, described in Table III, resulted in products having lower melting points than the original wax. Thus, Crown Wax at 6 per cent chlorine was much softer than the original wax; at 12 per cent chlorine, it resembled beeswax; at 25 per cent chlorine it was a thick liquid. Thus, any consistency between that of the original hard wax and a liquid can be attained by controlling the chlorine content of the product.

(5) *Progressive Chlorination of Hydrocarbons.*

A considerable series of progressive chlorinations was carried out; in part to secure information on the relationship between refractive index and chlorine content, so that the former constant could be of use in following future chlorinations; in part to study the effect of chlorine content on viscosity; and in part to evaluate stability in relation to chlorine content. It was found to be impractical to chlorinate Kensol 16 to 40 per cent content, because the viscosity of the product was too high for use as a Derminolnarben oil. Later, the question of chlorine content of Ultrax 20 in relation to compatibility with the several Igevins became important in formulating Derminol oil 1 analogues. Still further, we desired to test the accuracy of the opinion that the higher the chlorine content, the greater the stability. Several experiments will be described.

TABLE II

Chlorinations of Various Hydrocarbon Mixtures

Batch Designation	Hydrocarbon Mixture	Product g.	Cl %	Sp. Gr. 80°	Acid No.	Viscosity S.U.S. 54.4°
1	Diesel Oil	442	40.5	1.082	—	—
2	Diesel Oil	1583	40.4	1.092	—	—
3	Diesel Oil	2422	42.9	1.137	—	—
DO-4	Diesel Oil	2647	40.6	1.105	—	—
DO-5	Diesel Oil	2985	40.9	—	—	—
DO-6	Diesel Oil	2950	39.7	n^{100} 1.4871	—	—
DO-7	Diesel Oil	3095	37.5	n^{100} 1.5145	—	—
4	Heavy Alkylate	247	38.3	1.112	—	—
5	Heavy Alkylate	1922	35.3	1.078	—	—
6	Penn Crude Fr.	2456	35.7	1.096	—	—
7	Penn Crude Fr.	2442	37.4	1.141	—	—
PA-2	Penn Crude Fr.	2825	41.6	1.142	—	—
PA-3	Penn Crude Fr.	3050	43.5	1.179	—	—
PA-4	Penn Crude Fr.	4849	36.8	—	1.3	—
PA-5	Penn Crude Fr.	4441	35.5	—	1.7	—
PA-6	Penn Crude Fr.	4398	31.4	—	1.6	—
PA-7	Penn Crude Fr.	4365	40.2	—	2.0	—
PA-8	Penn Crude Fr.	4316	34.6	—	3.4	—
S-1	Synthol gas oil	490	41.9	n^{100} 1.5145	2.6	—
S-2	Synthol gas oil	1849	39.7	—	2.7	—
HFO-1	Hydrog. Fish Oil	1904	29.7	—	4.1	—
HFO-2	Hydrog. Fish Oil	2100	32.0	n^{100} 1.4948	4.1	—
K-16-1	Kensol 16	4323	33.3	n^{100} 1.4889	1.3	—
K-16-2	Kensol 16	4295	36.5	n^{100} —	1.2	—
K-22-1	Kendall C_{22-24}	4401	35.0	n^{100} 1.4960	2.8	—
HD-3	Hexadecane	—	40.7	n^{100} 1.4828	0.6	—
Nopco-4	Alkyl benzene	—	35.3	—	3.0	—
Ultrax 20	C_{19-20}	2200	29.4	n^{25} 1.475	0.6	73.7
Ultrax 20	C_{19-20}	2000	29.8	n^{25} 1.475	0.6	76.4
Ultrax 20	C_{19-20}	2700	37.0	n^{25} 1.484	—	165.2
Ultrax 20	C_{19-20}	2000	27.1	n^{25} 1.472	0.7	65.6
Ultrax 20	C_{19-20}	1500	26.8	n^{25} 1.472	—	67.6
Ultrax 20	C_{19-20}	2700	28.8	n^{25} 1.4759	—	74.4
Ultrax 20	C_{19-20}	2700	37.0	n^{25} 1.484	—	165.2
Ultrax 20	C_{19-20}	2000	28.3	—	0.4	74.5
Ultrax 20	C_{19-20}	7000	38.5	—	0.4	226.0
Ultrax 20	C_{19-20}	2500	30.3	—	0.4	87.2
Shell	C_{12-20}	1900	29.8	n^{25} 1.468	0.6	45.5
Shell	C_{12-20}	1500	41.6	n^{25} 1.489	0.7	99.0
Shell	C_{18-20}	700	38.7	n^{25} 1.487	0.7	210.0

Progressive Chlorination of Kensol 16.

Seven liters of Kensol 16 was chlorinated at 90° in a 6″ x 18″ glass jar with a 100 w. tungsten light as the sole catalyst, (Infra-red not used here.) At various stages of chlorination a one-liter portion of the charge was removed for

TABLE III

Chlorination of Waxes

Batch Designation	Wax Used	Charge g.	Product g.	Cl %	Acid: No.
SW-1	Superla	908	984	7.1	——
SW-2	Superla	931	1008	7.8	——
SW-3	Superla	922	1027	9.1	——
SW-4	Superla	1049	1170	11.7	——
SW-5	Superla	949	1074	12.2	——
CW-700-1	Crown Wax 700	148	157	5.6	——
CW-700-2	Crown Wax 700	140	154	7.9	——
CW-700-3	Crown Wax 700	608	774	14.7	0.22
CW-700-4	Crown Wax 700	608	819	25.0	0.21
CW-700-5	Crown Wax 700	3121	3355	7.1	0.53
CW-700-5A*	Crown Wax 700	——	——	26.7	——
CW-700-6	Crown Wax 700	2867	3056	6.3	1.0
CW-700-7	Crown Wax 700	3042	3845	19.8	——
CW-700-8	Crown Wax 700	——	3305	24.5	——
CW-1010	Crown Wax 1010	289	311	6.6	0
CW-1035	Crown Wax 1010	301	325	7.5	0.23
CW-A-1	Amorwax 1200 A	6000	——	11.9	0

*CW-700-5A rechlorinated.

examination. After the usual treatment with potassium carbonate, fat number determinations (heat at 95–100°) were made at 5 and 24 hrs., the results of the detailed examination being given in Table IV, in comparison with German DNO under similar treatment.

TABLE IV

Results of Chlorination of Kensol 16, with Analytical Data on Intermediate and Final Chlorination Products and on these Products after Five and Twenty-Four hour Fettzahl Determinations.

Spec. No.	Volatile at 95–100° (per cent) 5 hrs.	24 hrs.	Chlorine per cent Orig.	5 hr.	24 hr.	Acid Value 0 hr.	5 hr.	24 hr.	Iod. No.	n^{40}
Kensol-16—	—	—	—	—	—	—	—	—	—	1.4493
1	1.3	2.9	23.1	23.3	25.0	4.2	2.5	1.1	8.3	1.4761
2	0.9	3.0	32.5	33.3	33.5	2.1	1.3	1.1	4.2	1.4937
3	0.3	0.7	42.4	41.5	42.5	1.6	1.5	1.4	1.5	1.5104
4	0.2	0.4	44.9	45.0	45.2	1.6	1.4	1.3	1.1	1.5158
5	0.2	0.4	46.7	46.5	46.6	1.8	1.1	1.1	0.7	1.5187
DNO oil*	1.9	6.8	42.6	38.9	43.4	0.5	0.7	0.7	0.5	1.4831

*Authentic German DNO.

In Table IV loss in volatile matter was lower in all specimens of chlorinated Kensol 16 than in Derminolnarben oil. This could have been expected,

because Kogasin II, the raw material from which Derminolnarben oil was presumably made, contains hydrocarbons of chain length down to C_{10}. The decanes, monochloro-decanes, and similar materials are likely to be appreciably volatile at 95–100°. Comparing specimen 3 in Table IV with Derminolnarben oil, both having about the same chlorine contents, it is to be observed that the Kensol 16 product is only one-tenth as volatile in 24 hrs. as Derminolnarben oil. Further, there is little change in chlorine content with heating. Specimen 3, however, has three times the iodine number of the Derminolnarben oil. Specimens 1–5 show significant but decreasing iodine numbers. This evidence of unsaturation in products just out of chlorination operations is not simple to explain. It may be an evidence of loss of HCl from tertiary carbon substituted chloride, caused by either the temperature of chlorination (95–100)° or by the subsequent treatment with potassium carbonate. Double bonds thus created would add chlorine later to form 1,2-dichloro-addition products. The iodine number of the final product is only 0.7, which is about that of Derminolnarben oil.

Progressive Chlorination of Kensol 16 with Infrared Bulbs as Sources of Heat and Light.

In this experiment 2 liters of Kensol 16 was chlorinated in the all-glass apparatus previously described. The cylinder was heated with two infra-red bulbs (250 and 350 w. respectively.) The temperature of the cylinder and contents was maintained at 95–100° by adjusting the distance of the bulbs from the cylinder. No stirring was used, but rapid agitation of the contents of the cylinder was achieved by the introduction of chlorine and by the release of waste gases, mainly HCl, throughout the reaction mixture. Analytical data are shown in Table V.

TAVLE V

Chlorination of Kensol 16 under Infra-red Irradiation

Sample No.	Chlorine per cent	Acid No.	n^{40}
Kensol 16	0	0	1.4493
1	17.5	3.7	1.4683
2	24.7	4.2	1.4790
3	35.2	6.4	1.4968
4	42.0	5.6	1.5102
5	43.3	1.8	1.5173
6*	43.0	1.2	1.5167

*Specimen 5 after aeration and stirring with potassium carbonate.

Specimen 6 was lighter in color than the products in Table IV.

Progressive Chlorination of Hexadecane and Nopco Alkyl Benzene.

These hydrocarbons were chlorinated in order to prepare and study Derminolnarben oil analogues from specific types of hydrocarbons, it being assumed that these data would throw some light on the general problem of stability. Thus, pure hexadecane is representative of the straight chain hydrocarbons in Kogasin II; it had presumably been prepared synthetically from the C_{16} fraction of naturally occurring fatty acids; hence, its immediate value is of theoretical interest only; for economic reasons it is not practical. (It is to be noted, however, that subsequent to this work several relatively pure straight chain hydrocarbon fractions have become commercially available, i. e. Ultrax 20 and Shell C_{12-20} hydrocarbons.) Approximately 1800 g. of this material was chlorinated in the all-glass cylinder, described previously. Heating and light catalysis at 95°C. were accomplished by means of two infra-red lamps. About three days were required to introduce forty per cent of chlorine. In order that the data might be available for the analytical control of future chlorinations the refractive index was determined at chlorine contents of 21 and 31 per cent as well as on the final product.

At the conclusion of the chlorine introduction the product was aerated for 2 hrs. and then stirred with anhydrous potassium carbonate for an additional 4 hrs, the temperature being maintained at 95°C. Analytical data are shown in Table VI.

TABLE VI

Chlorination of Hexadecane

Sample No.	Chlorine per cent	Acid No.	n^{25}
Original	0.0	——	1.4313
1	21.9	——	1.4579
2	31.4	——	1.4723
3	40.7	0.6	1.4828

The final product was a nearly water-white oil, with a viscosity about equal to that of German DNO. This hexadecane analogue of DNO gave 5 hr. and 24 hr. Fettzahls (per cent residue after heating at 95–100° for these times) of 99.5 and 98 per cent respectively, in comparison with 98.1 and 93.2 which we obtained on authentic German DNO. The difference is explained in part by the fact that the German product was made from Kogasin II, which may contain hydrocarbons as low as C_{19}. The difference is not, therefore, necessarily a reflection of greater stability of our product.

The chlorination of Nopco alkyl benzene is followed in Table VII.

TABLE VII

Chlorination of Nopco Hydrocarbon
(Alkyl Benzene)

Sample No.	Chlorine per cent	Acid No.	n^{20}
Original	——	——	1.4961
1	22.7	9.0	1.5231
2	26.9	6.6	1.5309
3	32.7	6.4	1.5400
4*	35.3	3.0	1.5457

*After aerating and treatment with dry K_2CO_3 for several hours.

The chlorination was discontinued at 35.3 per cent because the viscosity even at this degree of chlorination was about equal to that of chlorinated Kensol 16 at 46 per cent. The product was dark colored but little if any darker than German DNO,—not too dark for practical use. The 5 and 24 hr. Fettzahls were 99.85 and 99.4 respectively, which indicate either high stability or low volatility at 100°, or both. However, the acid number of the final product, even after treatment with potassium carbonate at 95°, is high, which is interpreted as a reflection of instability. Thus, at 100° there may be a slow, constant loss of HCl under the influence of temperature and infra-red radiation. When the stirring is discontinued, the carbonate rapidly falls to the bottom, HCl is slowly evolved during cooling and shows up during the final titration with alkali. This explanation is to be regarded as speculative.

Progressive Chlorinations of Ultrax 20, *n-Dodecane*, *Butyl Stearate*, *n-Hexadecene*, *Nopco Alkyl Benzene and Kensol* 31x.

These chlorinations were made for varied purposes, but mainly to secure data on chlorine content vs. refractive index. In some instances stabilities and viscosities are included. The results are in Table VIII.

The high viscosity and low stability of Nopco Alkyl benzene at 30 per cent chlorine content and the satisfactory stabilities of chlorinated hexadecene and Kensol 31x are worthy of note.

(e) The Stabilities and Viscosities of Derminolnarben Oil Analogues and Certain Chlorinated Waxes

As a result of the first eighteen months of work on this project there had been accumulating a large series of chlorinated hydrocarbons and waxes, many of which had been screened in leather at Cincinnati. It seemed imperative to develop a test which would permit a comparison of the stability of these materials with the German products. It is admitted that results of such comparative tests may not be a true comparison of their stability in

TABLE VIII

Progressive Chlorination of Ultrax 20, n-Dodecane, Butyl Stearate, n-Hexadecene, Alkyl Benzene and Kensol 31x.

Product No.	Cl %	n^{28}	Acid No.	Viscosity S.U.S. 54.4°	Stability*
	Ultrax 20 Batch 1				
Original	——	1.4357	——	——	——
1	14.6	1.4509	——	——	——
2	21.5	1.4598	——	——	——
3	29.2	1.4707	——	——	——
4	36.2	1.4799	——	——	——
5	39.7*	1.4879	0.2	——	——
	Ultrax 20 Batch 2				
1	11.3	1.4660	——	——	——
2	25.4	1.4742	——	——	——
3	34.5*	1.4798	0.4	——	——
	n-Dodecane				
Original	——	1.4133	——	——	——
1	16.4	1.4312	——	——	——
2	28.3	1.4489	——	——	——
3	34.3	1.4592	0.9	——	——
4	42.7*	1.4762	0.5	——	——
	Butyl Stearate				
Original	——	1.4353	——	——	——
1	14.2	1.4530	——	——	——
2	23.7	1.4665	——	——	——
3	36.4	1.4879	——	——	——
4	40.2	1.4950	1.9	——	——
	Nopco Alkyl Benzene				
Original	——	——	——	——	——
1	16.1	1.5102	2.1	84.4	1.52
2	22.7	1.5203	2.1	174.6	2.28
3	26.0	1.5249	1.9	276.0	2.34
4	30.0*	1.5308	1.6	530.0	2.14
	n-Hexadecene				
Original	——	1.4336	——	——	——
1	31.9	1.4703	0.6	54.6	0.57
2	40.5*	1.4858	1.5	118.4	0.23
	Kensol 31x				
Original	——	1.4300	——	——	——
1	33.8	1.4793	0.4	48.8	0.77
2	44.6*	1.5035	0.5	233.0	0.78

*After treatment with potassium carbonate.
** % HCl liberated on heating 4 hrs. at 160°C. (See next section.)

military leather, but, to date, we have secured no data which would seem to invalidate the laboratory tests. The acquiring of a Saybolt Viscosimeter at this time also permitted determination of the viscosity of these products.

This physical constant we believe to be an important one in evaluating any product to be used in oiling and greasing leather.

Viscosity measurements were made by the procedure described in the ASTM specifications covering "Standard Methods for Test for Viscosity of Petroleum Products and Lubricants. ASTM Designation D88–38". Temperature was measured with a Saybolt thermometer graduated into tenths, the temperature used being 54.4°. For viscosities under 1000 seconds the universal tip was employed; above this viscosity the Furol tip was used.

We had considerable difficulty in developing a satisfactory method for determining stability. Obviously, any method employed is empirical, and is valuable for comparative purposes only, because we have no way of extrapolating the results obtained at high temperature into certain conclusions as regards actual stability in leather. In the production sheets of the Schultz-Schubert leather report [3], and in pamphlets published by I. G. Farben, it was noted that certain metallic ions, such as iron and copper, hastened the liberation of HCl and, hence, must be excluded from the product.

In developing our stability determination, we used a modification of that employed by the Hercules Powder Company who measure the per cent HCl liberated in 4 hours at 175° C. In their test a 25 g. specimen of the oil is heated at this temperature while a slow current of air is passed over the specimen to remove evolved HCl, which is collected in gas wash bottles containing standard alkali. We felt that a temperature of 175° is somewhat too drastic a treatment. Accordingly, we have adopted a temperature of 160° for our test. In earlier experiments we passed air through the oil, but, again, this proved too drastic, because active oxidation seems to promote the decomposition as, indeed, might be expected. Accordingly, the following procedure was set up. A hot air oven was constructed with openings for eight 200 x 32 mm. Pyrex test tubes. The temperature is maintained by relays of heaters controlled by a bi-metallic constant temperature regulator. The air is agitated with a fan which maintains even temperatures throughout the oven. A ten-gram specimen of test material is introduced into each test tube. A glass tube delivers a slow stream of air about 10–15 mm. above the surface of the sample. The air is in turn passed through two similar Pyrex tubes in series, the first containing 50 cc. of N/10 silver nitrate and the second 25 cc. of this reagent. Only occasionally does any HCl escape the first tube. Air is drawn through the battery of eight three-tube series by controlled suction. At the conclusion of the heating period, the contents of the two tubes containing silver nitrate are washed into a small flask, acidified with nitric acid and titrated with ammonium thiocyanate. The error introduced by not filtering the silver chloride was found to be negligible. The results of stability tests are shown in Table IX which follows.

It is difficult to draw more than general conclusions from the viscosities in Table IX. Generally speaking, viscosity increases with chlorine content

TABLE IX

Viscosities and Stabilities of Chlorinated Hydrocarbons and Waxes

Product	Per Cent Chlorine	Acid No.	Saybolt Viscosity 54.4°C.	Stability*
German DNO		1.43	95.3 S.U.S.	0.73
German DNO (Cincinnati)		1.48	90.2 S.U.S.	0.52
Diesel Oil No. 1	40.5	0.20	68.1 S.U.S.	0.32
Diesel Oil No. 2	40.4	0.15	78.6 S.U.S.	0.25
Diesel Oil No. 3	42.9	0.95	107.2 S.U.S.	0.38
Diesel Oil No. 5	40.9	0.35	87.3 S.U.S.	0.24
Diesel Oil No. 6	39.7	0.70	85.9 S.U.S.	0.28
Diesel Oil No. 7	37.5	1.30	63.7 S.U.S.	0.41
Kensol 16 1	23.1	0.63	53.5 S.U.S.	1.11
Kensol 16 2	32.5	0.50	124.5 S.U.S.	2.31
Kensol 16 3	42.4	0.60	645.0 S.U.S.	2.53
Kensol 16 4	44.9	0.54	128.0 S.F.S.	1.71
Kensol 16 5	46.7	0.47	191.7 S.F.S.	2.76
Kensol 16 (E.F.5)	39.6	0.68	304.0 S.U.S.	1.93
Kensol 16	45.3	1.39	134.8 S.F.S.	1.71
Kensol 16	43.0	1.60	772.0 S.U.S.	2.01
Kensol 16	38.6	0.40	319.0 S.U.S.	1.61
Hexadecane	31.4	0.66	54.5 S.U.S.	0.38
Hexadecane	40.7	0.60	107.5 S.U.S.	0.24
Ultrax 20	36.2	0.40	160.2 S.U.S.	0.14
Ultrax 20	39.7	0.20	241.0 S.U.S.	0.12
Ultrax 20	11.3	0.78	44.0 S.U.S.	0.18
Ultrax 20	25.4	0.64	64.5 S.U.S.	0.18
Ultrax 20	34.5	0.36	138.4 S.U.S.	0.20
Ultrax 20	28.4	0.66	78.9 S.U.S.	0.18
Dodecane	28.3	1.10	34.2 S.U.S.	0.36
Dodecane	34.3	0.90	38.2 S.U.S.	0.40
Dodecane	42.7	0.54	52.0 S.U.S.	0.36
Nopco Hydrocarbon	35.3	1.77	202.0 S.F.S.	2.22
Kendall C22-24	35.0	0.80	132.9 S.U.S.	1.81
Butyl Stearate	14.2	0.74	54.2 S.U.S.	0.70
Butyl Stearate	23.7	1.38	85.7 S.U.S.	0.31
Butyl Stearate	36.4	2.20	348.0 S.U.S.	0.45
Butyl Stearate	40.2	1.90	819.0 S.U.S.	0.45
Hydrogenated Fish Oil	29.7	4.10	256.0 S.F.S.	0.17
Hydrogenated Fish Oil	32.0	4.10	374.0 S.F.S.	0.23
Heavy Alkylate	38.3	0.51	350.0 S.U.S.	0.77
Heavy Alkylate	35.2	0.10	312.0 S.U.S.	1.94
Synthol Gas Oil	39.6	1.80	117.9 S.U.S.	2.50
Penn Crude Fract.	37.0	3.40	———	1.53
Crown Wax 700	25.3	———	———	0.27
Chlorafin-6**	5.9	———	———	0.11
Chlorafin-10	10.0	———	———	0.11
Chlorafin-15	15.1	———	———	0.14
Chlorafin-25	21.8	———	———	0.26
Chlorafin-35	28.1	———	———	0.27
Chlorafin-42	42.0	———	———	0.22
Chlorafin-42-S	42.0	———	———	0.17
Chlorafin-50	50.0	———	———	0.12
Amorwax-1200	11.8	———	———	0.11

**Chlorafins 42, 42-S and 50 are standard commercial products of the Hercules Powder Co., Parlin, N. J. Chlorafins 6, 10, 15, 25 and 35 were made by that company specifically for this project.

*Per cent HCl in 4 hrs. at 160°.

with any given hydrocarbon or hydrocarbon mixture. Since the viscosity requirements for maximum lubricating effect in fat-liquors and stuffing

mixtures are not known, and since the material we have been trying to match is Derminolnarben oil, we can tentatively adopt its viscosity as a yardstick and compare the viscosities of the other materials with that of Derminolnarben oil, which, in turn, is in the range of fish or neatsfoot oils. The average viscosity of the two specimens of Derminolnarben oil is 92.7 seconds. Seven specimens of Diesel oil analogues of chlorine contents varying from 37.5–42.9 per cent gave viscosities ranging from 63.7 to 107.2 sec. The lack of exact correlation between chlorine content and viscosity may be due to the fact that some of the specimens have lost HCl on standing with resultant production of olefinic bonds which would give a disproportionately low viscosity. Chlorinated hexadecane at 40.7 per cent chlorine gave a viscosity of 107.5 sec. Dodecane at 42.7 per cent chlorine gave only 52.0 sec. Ultrax-20, which is mainly C_{19-20} material, gave 241 sec. at 39.7 per cent chlorine. The increase here is due to increase in the length of carbon chain. The Kensol 16 series of chlorine contents from 23.1 to 46.7 per cent increased in viscosity rapidly, so that the products of chlorine content 44.9 and 46.7 per cent were run with the Furol tip. Kensol 16 contains approximately 20 per cent naphthenes and a similar amount of aromatics. The heavy alkylate fraction, consisting of branched chain material, gave a high viscosity, as did also the Synthol gas oil fraction. A series of chlorinated butyl stearates could still be read with the Universal tip at 40.2 per cent chlorine. Hydrogenated fish oil gave a very viscous Derminolnarben oil analogue. With a number of the products in Table IX in which series of chlorinations are described, we plotted chlorine content against viscosity and, from the curves, ascertained by interpolation the chlorine content necessary to give 92.7 S.U.S. These results are summarized in Table X.

TABLE X

Derminolnarben Oil Analogues. Chlorine Content Necessary to Match the Viscosity of Derminolnarben Oil.

Analogues	Approx. Chlorine content % required for 92.8 S. U. S.
Diesel oil	42.0
Dodecane	50.0*
Hexadecane	39.0
Ultrax 20	31.0
Kensol 16	31.0
Butyl Stearate	25.0

*By extrapolation.

The stability measurements in Table IX permit a number of conclusions, the most important of which is that if the hydrocarbon to be chlorinated is essentially straight chain, if it contains minimum amounts of naphthenes and branched chain material with hydrogens on tertiary carbon atoms, then

the product will be as stable as, or more stable than Derminolnarben oil. Products more stable than DNO are obviously to be desired. The following products give satisfactory stability: Diesel oil of Fischer-Tropsch origin; dodecane and hexadecane (laboratory chemicals only), butyl stearate, the entire series of Chlorafins (however, only those of lower chlorine content than 42 per cent satisfactorily penetrate leather) and Ultrax-20. Chlorinated Crown Wax 700 and Amorwax 1200A also were satisfactorily stable. Derminolnarben oil analogues from Kensol 16, Nopco hydrocarbon (branched chain alkyl benzene), Synthol gas oil fraction of American Fischer-Tropsch origin, heavy alkylate fraction, and a Penn. crude oil fraction are too unstable to lend hope that they are satisfactory products without modification or stabilizer.

(f). Attempts to Stabilize Derminolnarben Oil Analogues

The results in Table IX indicated that some of the hydrocarbons and all of the waxes tested gave chlorinated derivatives of satisfactory stability. Several of the hydrocarbon mixtures of unique composition gave products too unstable for practical use, although for a number of reasons they might be expected to have desirable qualities for leather. The cause of the instability, as noted previously, is largely the presence of chlorine atoms on carbons which spontaneously liberate HCl with the generation of olefinic bonds. Two methods of stabilizing these products occurred to us, namely, pre-treatment to remove labile chlorine and addition of stabilizers.

One type of pre-treatment is illustrated by the following experiment: A large specimen of Kensol 16, containing 46.7 per cent chlorine, was heated in a closed flask at about 150° while at the same time a current of nitrogen gas was passed through the oil. From time to time, specimens were removed and tested for chlorine content and stability (See Table XI). A similar experiment was carried out on chlorinated Nopco alkyl benzene. A charge of 600 g. was heated at 160° in a three-neck R. B. flask during constant stirring and aeration with nitrogen (See Table XI).

Both of the DNO analogues in Table XI lost chlorine as HCl became appreciably more stable to heat, and developed color. In the case of Nopco DNO the viscosity fell decidedly, supporting the view that olefinic bonds are formed. These products were not tested in leather.

In another type of pretreatment a specimen of DNO from Diesel oil was stirred with dry potassium carbonate for several hours at 135°. Little change in chlorine content or stability occurred. This method should be further explored, possibly with the use of higher temperatures.

It would appear from the preceding results that heat or suitable chemical treatment can be employed to prepare stable DNO analogues. This might be practically accomplished by over-chlorination, i. e., chlorinating to a higher chlorine content than desired, removal of the labile chlorine, and decolorizing, if necessary. The olefinic bonds do not appear to be objectionable.

TABLE XI

Stability of Kensol 16 and Nopco Analogues of Derminolnarben Oil, Following Heating to Removed Labile Chlorine

Time of Heating Hrs.	Cl Per cent	Stability*	Viscosity S.U.S. 54.4°
	Kensol 16,150°		
0	46.7	2.76	——
4	——	1.09	——
8	44.1	0.86	——
12	43.9	0.70	——
16	43.3	0.66	——
	Nopco Alkyl Benzene, 160°		
0	35.3	2.15	202
8	31.3	0.43	159
12	31.5	0.29	159
16	31.3	0.23	160

*HCl liberated in 4 hrs. at 160°.

In June and July 1948, a series of tests was begun to evaluate certain stabilizers which could be added in small amounts to DNO analogues to inhibit formation of HCl. Acid number determinations were made at the start of the experiment and approximately a year later. The results are given in Table XII.

Satisfactory stabilizing effects are shown by hexadecylamine at 0.2 per cent conc., phenoxypropylene oxide, epichlorhydrin, urotropin, dibutyl tin laurate, pyridine, Alkaterage C and triethanolamine. The following materials were detrimental: hexadecylamine at 1 per cent conc., and ammonium acetate.

Summary

(1). A series of hydrocarbon mixtures and waxes (high-melting hydrocarbons) of widely varying composition, and including specimens of German and American-made Fischer-Tropsch hydrocarbons, have been chlorinated in the course of preparing analogues of Derminolnarben oil and Derminol fat 1.

(2). In many instances progessive chlorinations were carried out in order to study the effect of chlorine content on refractive index, Saybolt viscosity and stability.

(3). The following chlorine contents were found to be necessary to match the viscosity of German DNO: Diesel oil, 42 per cent; dodecane, 50 per cent; Kensol 16, 31 per cent; hexadecane, 39 per cent; butyl stearate, 25 per cent; and Ultrax 20, 31 per cent.

TABLE XII

The Effectiveness of Added Stabilizers on the Liberation of Acid from Derminolnarben Oil Analogues

Derminolnarben Oil Analogue	Date Tested	Acid No.	Date Tested	Acid No.
		0.2% Hexadecyl Amine		
Kensol 16, 39.6% Cl	7/8/48	1.09	7/29/49	1.31*
Ultrax 20, 39.7% Cl	"	0.69	"	0.53*
Diesel Oil-6, 39.7% Cl	"	0.97	"	0.84*
Hexadecane, 40.7% Cl	"	0.79	"	0.53*
		1.0% Hexadecyl Amine		
Kensol 16, 39.6% Cl	7/9/48	2.28	"	3.54
Ultrax 20, 39.7% Cl	"	0.77	"	1.83
Diesel Oil 6, 39.7% Cl	"	1.78	"	2.12
Hexadecane, 40.7% Cl	"	1.16	"	1.88
		0.5% Ammonium Acetate		
Kensol 16, 39.6% Cl	6/28/48	0.70	7/27/49	6.05
Ultrax 20, 39.7% Cl	"	0.70	"	2.51
Diesel Oil -6, 39.7% Cl	"	1.01	"	3.44
Hexadecane, 40.7% Cl	"	0.40	"	1.59
		0.2% Phenoxypropylene Oxide		
Kensol 16, 39.6% Cl	7/30/48	0.82	"	1.11*
Ultrax, 20 39.7% Cl	"	0.44	"	0.22*
Diesel Oil -6, 39.7% Cl	"	0.99	"	1.23*
Hexadecane, 40.7% Cl	"	0.46	"	0.33*
		0.2% Epichlorohydrin		
Ultrax 20, 39.7% Cl	6/25/48	0.35	1/14/50	0.22*
Diesel Oil -6, 39.7% Cl	"	1.06	"	0.54*
Hexadecane, 40.7% Cl	"	0.34	"	0.50*
Kensol 16, 39.7% Cl	"	0.67	"	0.77*
Derminol Fat II	"	0.30	"	0.30*
Derminol Oil I	"	0.52	"	0.67*
		0.5% Urotropin		
Ultrax 20, 39.7% Cl	6/23/48	0.31	12/30/49	0.55*
Kensol 16, 39.6% Cl	"	0.60	1/14/50	0.51*
Diesel Oil -6, 39.7% Cl	"	1.09	12/30/49	0.43*
Hexadecane, 40.7% Cl	"	0.45	"	0.29*
		0.2% Dibutyl Tin Laurate		
Derminol Fat II	11/5/48	0.64	1/18/50	0.98*
Derminol Oil I	10/25/48	0.72	12/30/49	0.82*
		0.1% Pyridine		
Kensol 16, 39.6% Cl	6/25/48	1.06	1/14/50	0.74*
Ultrax 20, 39.7% Cl	"	0.38	"	0.41*
Hexadecane, 40.7% Cl	"	0.39	"	0.27*
		0.2% Alkaterage C		
Kensol 16, 39.6% Cl	6/18/48	0.95	1/14/50	0.98*
Ultrax 20, 39.7% Cl	"	0.31	"	0.45*
Diesel Oil -6, 39.7% Cl	"	0.78	"	0.72*
Hexadecane, 40.7% Cl	"	0.34	"	0.50*
		0.2% Triethanolamine		
Derminol Fat II	10/27/48	0.69	1/18/50	1.02*
Derminol Oil I	10/25/48	0.44	12/30/49	0.59*

*Satisfactory Stability.

(4). Hydrocarbon mixtures containing important amounts of branched chain hydrocarbons and naphthenes were found to be too unstable for incorporation in leather without addition of stabilizer.

(5). Straight chain hydrocarbons such as n-dodecane, n-hexadecane, and Ultrax 20 gave chlorinated derivatives more stable than German DNO. Diesel oil gave a product of stability equal to that of DNO. All chlorinated waxes studied showed satisfactory stability.

(6). From its composition, it is believed that Shell C_{12-20} hydrocarbon will yield a DNO of satisfactory stability.

(7). A series of Derminolnarben oil analogues with added stabilizers was allowed to stand for about one year and tested for change in acid number. The following compounds showed definite stabilizing values; hexadecyl amine, 0.2 per cent; phenoxypropylene oxide; epichlorhydrin; urotropin; dibutyl tin laurate; alkaterage C; and triethanolamine.

(8). Several hydrocarbon mixtures were overchlorinated and heated to remove labile chlorine; the resulting products showed improved stability.

(9). DNO analogues from many of the hydrocarbon mixtures and the chlorinated waxes described above have been found[7] to be satisfactory fat-liquoring and stuffing agents in upper leathers. These appear, further, to withstand storage in leather without evidence of deterioration.

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The Thermal Stability of Leather

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Introduction

The influence of heat on leather has been widely discussed regarding the shrinkage of hide or leather in hot water. When a small strip of fresh hide is placed in water and the temperature is gradually raised, the hide elongates

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slightly at first and then contracts. Mineral tannages usually make leather that can be heated in water near the boiling point before contraction occurs, whereas with the best vegetable tanned leathers it occurs near 85°C. Oil tanned leather, on the other hand, does not differ markedly from untanned collagen in that shrinkage occurs near 60°C., but Hobbs [1] reported that it contracts at a much slower rate and when allowed to dry after boiling, most of the original softness and flexibility is retained.

It has long been known that the prolonged action of water in the presence of heat or acids and bases will dissolve collagen. Leather reacts in a like manner, but at a slower rate. It is apparent, then, that a study of the shrinkage of hide or leather in water does not in the strictest sense measure the heat resistivity of leather. Similarly, measurement of the changes in length of leather or collagen in hot air, [2] or any chemically active heat transfer medium, introduces other factors in addition to heat alone. If a comparatively inert heat transfer medium such as paraffin oil is used, a clearer picture of the effect of heat may be gained, and the influence of other factors can be more easily interpreted.

Hough [3] has discussed the merits of chrome and vegetable tanned leather regarding thermal stability of leather for use in oil seals. He concluded that vegetable tanned leather is more resistant to dry heating, but is badly damaged if moisture is present. Contrastingly, chrome tanned leather resists higher temperatures under moist conditions but suffers serious deterioration by dry heat. A chrome-vegetable retan leather, in general, exhibits the combined advantage of the two tannages.

To obtain additional data on those factors which influence the chemical and physical stability of mechanical leather under the dynamics of use and changes in temperature the present investigation was undertaken. It applies especially to heat resistant leather for use in oil seals.

Experimental

The type of tannage used can alter the thermal stability of collagen. In order to evaluate such changes, three general methods of test were employed. Area and volume changes of commercial chrome-vegetable retan mechanical leathers, vegetable tanned leather and chrome tanned leather after treatment in hot oil were measured, shrinkage temperatures of the leathers in glycerol-water solution and in paraffin oil as well as in other lubricants were determined, and the change in strength of some of the leathers as a result of heat treatment was measured. These tests were designed to find how leather is effected by heat, and how this effect can be modified. In the course of investigating the effect of different tanning materials was also considered.

Area and Volume Changes

Samples of leather of uniform initial area were selected and immersed in a heat transfer medium. After heating at a particular temperature range for a

given period of time, they were removed, cooled, freed of the heat transfer medium, allowed to dry in air and measured for area and volume changes.

Shrinkage Temperature Methods

Changes in the length of the samples were measured as a function of temperature on the Theis shrinkage meter [4]. The standard A. L. C. A shrinkage determination procedure [5] was followed as a basic procedure. Furthermore, the entire temperature-meter reading curve was secured from room temperature to almost 200°C., keeping the heating rate constant at 3 to 7°C. per minute. From this curve the equilibrium temperature at which the preliminary sample elongation ceased was noted, as well as the temperature range during which the sample shrunk 1 mm.

Strength Measurements

The strength of leather may be conveniently determined by measuring the force required to push a small ball-pointed rod through a sample. An apparatus [6] for such a test was used in some instances to determine strength changes which occurred.

Experimental Results

Commercial chrome-vegetable retan mechanical leathers heated in paraffin oil above 140°C. for 48 hours or longer showed, in general, 10–14 per cent area shrinkage and 14–18 per cent volume shrinkage as is shown in Table I. The volume exceeds that of the area loss because during the heating the thickness decreased by 4 per cent. Under similar conditions, chrome tanned leather showed nearly 50 per cent area loss, whereas vegetable tanned leather showed only 6–8 per cent area loss. Using commercial gear lubricants and other automobile lubricants as heat transfer media resulted in no appreciable difference in area changes of the leather than that obtained with the paraffin oil. The paraffin oil selected for the heat transfer medium given in Table I and mentioned in the Tables to follow for both conditioning leather and for determining shrinkage temperature was a heavy white paraffin oil of 335/350 viscosity.

Lubricants and Tannages

Using the standard A. L. C. A. method for determining shrinkage temperature and oils instead of glycerol-water solution, the shrinkage temperatures of a chrome-vegetable retan mechanical leather were measured in six different lubricants but little or no difference was observed in the initial shrinkage temperature as is shown in the upper part of Table II. However, as would be expected from the area stability tests given in Table I the type of tannage given by the various tanners does influence the initial shrinkage temperature in oil as is observed in the lower part of Table II.

TABLE I

Area and Volume Changes of Leather Heated in Oils

Leather	Gear Lubricant "A" 140 – 150°C. 72 Hours		Paraffin Oil 140 – 150°C. 48 Hours		Paraffin Oil 135 – 140° C. Two Weeks		Paraffin Oil 135 – 140°C. Four Weeks	
	% Area Decrease	% Volume Decrease	% Area Decrease	% Volume Decrease	% Area Decrease	% Volume Decrease	% Area Decrease	% Volume Decrease
Retan A	12.3	15.1	14.2	18.4	10.0	12.3	13.0	15.8
Retan B	12.3	12.4	15.6	17.4	11.0	13.1	14.7	20.3
Retan C	12.3	12.3	14.2	15.5	10.0	11.8	13.3	15.7
Retan D	10.7	13.2	14.2	18.8	11.0	14.5	14.0	18.3
Retan E	10.7	12.0	14.2	17.6				
Vegetable	6.0	9.2	8.4	12.7				
Chrome			48.8	50.3				

Gear Lubricant "A"—Suitable viscosity and cold test to meet the viscosity and channelling requirement of S. A. E. 90 Hypoid.

Paraffin Oil—Heavy white paraffin oil (335/350 viscosity).

TABLE II

Shrinkage Temperature of Retan Leather "A" in Various Lubricants.

Lubricant	mm Expansion	Initial Shrinkage Temperature °C	After 1 mm Shrinkage	Shrink Time (Minutes)
Gear Lubricant "A"	1.46	127	148	7.00
Gear Lubricant "B"	0.40	129	165	8.10
Gear Lubricant "C"	0.90	128	148	6.65
Hydramatic Transmission Oil	0.66	128	154	8.65
Hydraulic Oil	8.63	127	162	11.65
Paraffin Oil	1.03	129	148	6.33

Gear Lubricants A, B and C were commercial Hypoid Gear Oils for use in rear axles of automobiles and of suitable viscosity and cold-test to meet the viscosity and channelling requirements of S. A. E. 90 Hypoid.

Shrinkage Temperature of Retan Leathers in Gear Lubricant "A".

Leather	mm Expansion	Initial Shrinkage Temperature	After 1 mm Shrinkage
A	1.46	127	148
B	0.30	138	167
C	0.17	125	151
D	0.93	130	151
E	0.23	130	151

Influence of Preheating on Shrinkage

Some samples of retan mechanical leather were heated in paraffin oil at 140–150°C. for varying periods of time while other samples were heated in air at 95°C. to obtain an indication of the influence of preshrinkage prior to using the leather for oil seal purposes. Table III shows the wet and dry shrinkage temperatures of the leather samples after they had been heated in paraffin oil at 140–150°C. for the time periods given. The heat treatment has a definite influence on the wet shrinkage of the leather as is seen in the data on area and volume changes in the upper part of the table. The initial wet shrinkage temperature while originally high, decreases noticeably up through 48 hours of treament in oil at 140–150°C. and does not recover to a high wet shrinkage temperature until some 336 hours of preheating. The dry shrinkage temperature is high before treatment and becomes higher as a result of the preheating in paraffin oil. The pretreatment of the leather in paraffin oil for even a few hours definitely improves the thermal stability of the leather to hot oil.

TABLE III

The Shrinkage of Retan Leather in Glycerol-Water Solution after Conditioning in Paraffin Oil at 140 - 150°C. for Varying Periods.

Hours Conditioned	mm. Expansion	Initial Shrinkage Temp °C.	After 1 mm. Shrinkage °C.	Shrink Time Minutes	% Area Decrease	% Volume Decrease
0	0.20	113.0	>115.0	1.45	——	——
0.1	0.30	101.0	107.5	1.55	6.7	8.8
2.0	1.00	76.0	87.0	2.22	9.7	12.8
32.0	0.00	76.8	94.8	1.40	11.4	15.4
48.0	0.16	90.0	>115.0	7.16	14.7	15.5
336.0	0.30	>115.0	——	——	10.0	13.2
672.0	0.05	>115.0	——	——	13.3	15.7

Shrinkage Temperature of Retan Leather in Paraffin Oil After Conditioning in Paraffin Oil at 140 - 150°C. for Varying Periods.

Hours Conditioned	mm. Expansion	Initial Shrinkage Temp °C.	After 1 mm. Shrinkage °C.	Shrink Time Minutes
0	0.33	127.0	164.0	10.00
0.1	0.30	140.0	196.0	18.23
2.0	2.00	147.0	187.0	10.96
32.0	0.56	153.0	195.0	15.00
48.0	0.40	149.0	194.0	17.64
336.0	0.80	157.0	200.0	11.85
672.0	0.73	147.0	197.0	18.00

The data on the samples of retan mechanical leather heated in air at 95°C. for varying periods of time is given in Table IV. Examination of the data

and a comparison of it with the data in Table III shows that the preheat treatment of the leather in air has a harmful influence on the thermal stability of the leather in oil.

TABLE IV

The Shrinkage of Retan Leather in Glycerol-Water Solution after Conditioning in a Drying Oven at 95°C.

Hours Conditioned	mm. Expansion	Initial Shrinkage Temp. °C.	After 1 mm. Shrinkage °C.	Shrink Time Minutes	% Δ Area
0	0.20	113.0	>115.0	1.45	——
0.1	0.19	114.0	>115.0	1.58	1.7
1.0	0.37	100.5	111.0	2.53	11.4
2.0	0.20	85.0	97.0	2.60	12.3
8.0	0.06	78.0	95.0	3.37	14.9
16.0	0.00	71.8	98.0	5.22	15.4
21.0	0.00	71.5	95.0	4.90	10.7
45.0	0.01	70.6	90.4	4.00	13.0
92.0	0.00	66.5	91.8	4.85	——

Shrinkage Temperature of Retan Leather in Paraffin Oil after Conditioning in a Drying Oven at 95°C.

Hours Conditioned	mm. Expansion	Initial Shrinkage Temp. °C.	After 1 mm. Shrinkage °C.	Shrink Time Minutes
0	0.33	127.0	164.0	10.0
0.1	0.10	126.5	170.0	13.2
1.0	0.17	113.0	155.0	8.5
2.0	0.17	109.0	160.0	12.4
8.0	0.10	98.0	123.3	4.2
16.0	0.07	97.0	118.0	3.1
21.0	——	95.0	122.5	4.4
45.0	0.10	91.0	111.5	3.8
92.0	0.13	86.5	114.0	4.1

Strength Changes

Samples of leather including chrome, vegetable, chrome-vegetable retan, syntan, and sulfonyl chloride-vegetable retan tannages were measured for puncture resistance before and after thermal treatment. Air, glycerol-water solution, and paraffin oil were employed as heat transfer media. The influence of type of tannage and type of treatment is shown by the data in Table V. An analysis of variance was made to determine the significance of the data and there was a real difference between tannage and treatment. Examination of the data in the table shows that a vegetable tannage does not afford as much resistance to heat as does a chrome tannage or a chrome-vegetable

retannage from the standpoint of heat treatment in air, glycerol-water solution or in oil.

TABLE V

Pounds Force Required to Puncture Leather Before and After Different Heat Treatments.

Tannage	Control	24 Hours in Air at 95°C.	Control	6 Hours in Glycerol-Water Solution at 95°C.	Control	24 Hours in Paraffin Oil at 95°C.
Vegetable	90	82	88	11	62	35
Chrome	139	115	105	119	110	167
Chrome-Vegetable Retan	173	159	150	129	197	151
Sulfonyl Chloride-Vegetable Retan	118	99	106	61	107	143
2,4 - DB Synthetic	87	71	106	21	89	95
2,4 - DF Synthetic	104	66	86	20	56	59
2,4 - DB Synthetic Over Chrome	145	59	127	110	110	98

2,4 – DB Synthetic is the Condensation Product of Resorcinol and Benzaldehyde.
2,4 – DF Synthetic is the Condensation Product of Resorcinol and Furfural.

Aging Characteristics

Two groups of sulfonyl chloride-vegetable retan leather were heated 48 hours at 95°C., one in air and the other in paraffin oil. They were then soaked in chloroform overnight and allowed to dry in air. The two groups were then thoroughly wetted with water, drained and stored while wet for over six months in sealed bottles. At the end of that time, puncture tests showed that samples of the group heated in air suffered appreciable breakdown in strength during aging. Those heated in the paraffin oil did not show any appreciable change in strength as is shown in Table VI. For a comparison with the puncture resistance of the original leather compare the values of the sulfonyl chloride-vegetable retan leather in Table V. Preheating in oil not only gives much better heat resistance than preheating in air but also gives a leather which does not show any appreciable change in strength as a result of preheating.

Summary

The influence of heat on leather has been studied with particular regard to the stability of the leather in oil. Paraffin oil was chosen as the heat transfer medium while air and glycerol-water solution were used in some cases.

Chrome tanned leather shrinks rapidly in oil above 100°C. while vegetable tanned and chrome-vegetable retanned leathers shrink slower and show considerably less shrinkage. Chrome tanned leather, chrome-vegetable retanned

TABLE VI

Influence of Aging on Puncture Resistance of Thermally Treated Sulfonyl-Chloride Vegetable Retan Leather.

Samples for Aging Tests were taken immediately adjacent to one another.

Sample	Heated 48 Hours in Air at 95°C.	Heated 48 Hours in Paraffin Oil at 95°C.
1	33	101
2	41	102
3	39	98
4	35	102
5	51	106
6	51	111

Ageing—Both sets of samples were thoroughly wetted with water after Thermal Treatment. The water was drained off, and the leather samples while wet were stored in sealed bottles for over six months.

leather, and some syntanned leathers also shrink near 100°C. in water, whereas the vegetable tanned leather shrinks at 85°C. or lower.

Heat apparently conditions leather so that it tends to oppose shrinkage when subsequently reheated. This opposition to shrinking falls off rapidly with time in the case of leather heated in hot air but with leather heated in paraffin oil it falls off very slowly and requires several months in some cases.

Hot air seems to be more detrimental to leather than hot oil. Both can cause a weakening of the fiber structure of leather. The presence of chrome in the leather resists the weakening effect of the heat upon the fiber strength.

Conclusion

The thermal stability of leather seems to be a fundamental property of the hide substance and the type of tannage. For oil seal leather, a combination tannage offers the optimum heat resistivity with little change in strength. Shrinkage of leather for oil seals can be almost completely stopped by conditioning the leather in paraffin oil at 100°C. for a few hours before molding and manufacturing the finished product.

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ABSTRACTS

Vegetable Tanned Leather Analysis Committee. Progress Report No. 3. By G. Forsyth. *J. Soc. Leather Trades' Chemists*, **36,** 170 (1952). The method of determining all soluble salts as sulfates in the sulfated ash of the water soluble matter is discussed briefly. The object of the test is to give some indication of the liability of the leather to spue due to excessive amounts of soluble inorganic salts. The committee points out that the test can have only limited value for several reasons. For example, many manufacturers deliberately add considerable quantities of certain metallic salts. The test makes no distinction, in used leather, between the original salts and the salts derived from perspiration. Nor does the test discriminate between different salts. All salts do not have the same tendency to give rise to spue. There has been considerable interest in the Australian method (Cox) for rapid determination of water soluble matter. In brief the method consists in shaking leather shavings (not petroleum ether extracted) with 50 times their weight of water at 45 degrees C. for 90 min., then evaporating an aliquot portion and weighing the soluble matter. Figures obtained are close to, but slightly lower than, official method results. The committee intends to investigate the Reed-Churchill method. (*This Journal*, **14,** 133 (1919)). R. H. T.

The Heats of Wetting of Hide Substance Between Zero and Sixty Degrees Centigrade. By H. G. Wollenberg. *J. Soc. Leather Trades' Chemists*, **36,** 172 (1952). The heat of wetting of dry collagen is important. Recently foot health advantages of leather by demonstration of thermostatic effects have been emphasized. For this study samples were made of normally limed butt, which had been delimed with ammonium chloride and brought to a pH 5.7 with HCl, fresh green hide and green hide which had been kept in 10 per cent sodium chloride solution for 5 weeks. All were degreased and dried by acetone recycling and then evacuated at 103 degrees C. for 16 hours. Part of these were converted to shrunk samples by immersion in a minimum of water at 75 degrees C. for 5 min. They were then acetone dehydrated and dried as before. The product was a gelatin powder of high strength, over 200 g. Bloom, minus 42 mesh and pH 6.0. A table of nitrogen, ash and shrink temperatures of the samples is given. The calorimeter used is described. A gelatin powder (42 mesh, 200 g. Bloom) was included in the tests. Determinations were made at approximately 0, 20, 40 and 60 degrees C. Heats of wetting of unshrunk pelts show a strong temperature dependence, more so than in the shrunken condition. The results vary from 49 cal/g. at zero degrees to about about 16.5 cal/g. at 60 degrees C. for normal, and from 38 cal/g. at zero degrees to 16 cal/g. at 60 degrees for shrunk pelt. All approach the same level at 60 degrees C. Some theoretical considerations of the phenomena of adsorption and of wetting by immersion are considered, and other methods of evaluation of heats of adsorption briefly referred to. An explanation is put forward for the observed temperature dependence of heats of wetting of the different collagens used. For a practical interpretation the author assumes a pair of shoes is left to dry near a fire and that the leather does dry out completely. They are put on after a few minutes cooling and worn directly into the rain. If the shoes are completely wet, the temperature will rise by 39 degrees C. and the final temperature rise so high, about 58 degrees C., that the wearer would be obliged to remove them. R. H. T.

The Function of the Carboxyl Group of Collagen in the Fixation of Cationic Chromium Complexes as Shown by the Behaviour of Carboxylic Type Cationic Exchangers Towards Chromium Compounds. By K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **36,** 182 (1952). Two principal methods are used in the study of chromium complexes with ion exchangers. First there is the equilibrium method using an exchange resin with a capacity greatly exceeding the amount of ions exchangeable; and secondly the

non-equilibrium method in which the contact is for various times (depending upon the stability of the chromium compounds) between chromium compounds containing cations in large excess of the exchange capacity of the resins. The latter is similar to the chrome tanning bath and can be used in the study of some special aspects of the reactivity of chromium compounds. Chrome tanning compounds ordinarily used are mainly positively charged. Until fairly recently the cation exchangers have been of good quality and the anion exchangers inferior. Now strongly basic quaternary anion exchangers of good quality are available. Since carboxyl groups supposedly are the main groups involved in the fixation of cationic chromium complexes by collagen, the exchange of cationic chromium by means of the carboxylic type of exchangers under conditions akin to those of tanning should be more comparable with the chrome tanning process than the use of the sulfonic acid type of resin. The present paper contains a summary of some of the results obtained with various chromium salts using hide powder and also a resin with a carboxyl as the functional group (Amberlite IRC-50) as substrates. The amounts of sodium taken up by Amberlite IRC-50 and a sulfonated crosslinked polystyrene, Dowex -50, at complete pH range are compared. In the carboxylic resin the carboxyl is present in the unionized condition at pH below 4 and is not completely ionized until it passes to the alkaline side. The sulfonic acid group of the sulfonate resin is fully ionized over the entire range of pH 2-12. At pH 6-7 the carboxylic resin is similar to collagen under the conditions of chrome tanning. Competition of the hydrogen ions for the carboxyl ion is marked at high concentration of hydrogen ions. The carboxyls of the resin penetrate into the chromium complexes, displacing complexly held acid groups such as the sulfato group. The carboxyls of collagen do not displace sulfato groups of the chromium complexes, since the acidity of the sulfato-chromium fixed by the collagen is identical with the acidity of the original sulfato-chromium cations of the solution. Shuttleworth's experiments with solutions of sodium acetate-chrome alum are shown not to be an appropriate model of the system, collagen-chromium salts. In many respects collagen and the resin show a striking similarity in their reactions with basic chromium chlorides and sulfates, containing cationic chromium as the dominating constituent. These findings support the concept that the ordinary chrome tanning process principally involves carboxyl ions of collagen and electropositive chromium complexes. In examining solutions of chromium salts containing cationic as well as anionic and non-ionic complexes divergences between the reactivities of the carboxylic resin and collagen are shown. The probable reason is the fact that the resin is strictly restricted to cationic chromium, whereas the hide protein can react with and irreversibly bind non-ionic and anionic chromium. This difference behaviour is particularly well illustrated by the reaction of extremely basic chromium chlorides with the two substrates; the resin fixes very small amounts of chromium on account of the predominating non-ionic chromium, whereas collagen shows a very large chrome uptake as the result of the participation of non-ionic valency forces of the protein in the fixation of aggregated non-ionic complexes. The contrasting influence of the age of diluted chrome liquors (content of non-ionic chromium) upon the chrome uptake by the resin and by collagen is another striking illustration of the theoretical implications of dissimilarity of the systems. The speculative view claiming chromium complexes, irrespective of their sign of charge, to be attached to collagen by means of its carboxyl groups appears difficult to reconcile with the results obtained in experiment with the non-ionic phthalo-sulfato-chromium complexes, tetra-oxalatodiol-chromiate, and hexathiocyanato-chromiate, which two latter compounds are typical anionic complexes. Although the phthalato complex is inert towards the carboxyl of the resin, it possesses marked affinity for collagen, exerting tanning action. The results are considered as constituting additional evidence indicating the importance of the constitutional factors of the chromium complexes in tanning, and of the governing function of the carboxyl ion of collagen for its fixation of cationic chromium complexes. R. H. T.

Report of the Physical Testing of Leather Committee. By R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **36**, 206 (1952). For the measurements of buckle tear loads, corrections are given which cover how much of the specimen should protrude from the jaws of the testing machine. An official cracking test for the grain of heavy leathers is recommended. The principle of the test is the observance of cracking when leather is bent, grain outward, around a mandrel of known diameter, the force applied being the least required to maintain the leather and mandrel in contact. A description of the apparatus is given. Various sizes of mandrels with standard diameters are given. The diameters are numbered (n). A crack index is obtained from the diameter of the mandrel (n) multiplied by the thickness (t), the index therefore being (nt). R. H. T.

A Note on the Spectrophotometric Methods of Tannin Analysis for Black Wattle Tannins. By D. G. Roux. *J. Soc. Leather Trades' Chemists*, **36**, 210 (1952). Water soluble gums as well as sucrose have been found in black wattle extracts. These gums give water white solutions and will not interfere with the ferrous tartrate colorimetric method of tannin analysis. As the light absorption characteristics of such compounds are unknown, an investigation was made to see whether they would interfere with the spectrophotometric methods of tannin analysis. From the results obtained the conclusion is drawn that they will not interfere. R. H. T.

The Tannins of Certain Eucalypt Species and Pinus Radiata. By H. Anderson. *J. Soc. Leather Trades' Chemists*, **36**, 211 (1952). Past investigations indicate that the species available in Australia in sufficient supply do not give good tanning extracts, and those of good quality are not available in sufficient quantity. Therefore the only hope of finding new tanning products for commercial use lies in the byproducts from existing timber industries. The economic possibilities of recovering tannins from the eucalyptus species used in pulp manufacture are discussed with the conclusion that such a procedure is feasible under the right conditions. The bark of the lower trunk of the Pinus Radiata is quite rich in tannin. Fortunately the industrial procedure is such that segregation of this rich bark would not be too difficult. Hence it becomes a possible source of tannin. Extraction and effect of sulfiting are discussed. R. H. T.

The Chemical and Physiological Properties of Sodium Silicofluoride as Used in the Treatment of Hides and Skins. By C. C. Kritzinger. *J. Soc. Leather Trades' Chemists*, **36**, 217 (1952). Sodium silicofluoride (sodium fluosilicate) has greatly reduced the loss due to damage to hides by insect pests, such as hide and skin beetles and the skin moth, in South Africa. In this paper information on the chemical sodium silicofluoride, is given. Others to follow will give detailed accounts of methods evolved for its application during curing, storing and tanning. Commercial sodium silicofluoride (Na_2SiF_6) is a by-product of the phosphate industry and is available in S. Africa as a paste, 12 per cent moisture, and as a dry powder of 98 per cent minimum purity. It is an ordorless, white crystalline salt, nonhygroscopic although gathering enough moisture to become lumpy at relative humidities of over 90 per cent. It is soluble in water to the extent of only 0.65 per cent at room temperature but increases to 2.45 per cent at 100 degrees C. Its solubility is increased by ammonium sulfate and phosphoric acid but decreased by sodium sulfate and chloride. Both cationic and anionic surface active agents increase the stability of its suspensions but anionic agents do not appear to be effective. Solutions have a pH of 3.5 due to hydrolysis, hence the concentration may be determined by direct titration with phenolphthalein as an indicator. The acidity is readily buffered with the result that there is no undue

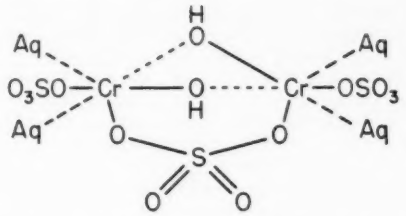
hide swelling due to acidity. Wet salted hides treated with the silicofluoride show less loss of weight from green to cured condition than untreated hides. It seems to assist bating through a dispersive action on the cementing globular proteins, however, it does not adversely affect the fibrous protein and the physical properties of the leather. Growth of bacteria on steer hides can be prevented by dipping in saturated solutions of silicofluoride. This is true for bacteria resistant to sodium chloride. As a result, it prevents red-heat and other stains. It also shows good protection against molds. For insect control it is superior to arsenicals because cheaper, acts both as stomach and contact poison, kills more rapidly, is less toxic to humans and is toxic to a wide range of insects. When hides are treated with sodium silicofluoride the activities of rodents practically ceases. Thin layers of the powder spread around rodent breeding places give good results. While less toxic than arsenic it does attack mucous membrane, causing temporary watering of the eyes and nasal discharge. No dermatitis has been noted either in practice or in deliberate attempts to induce it experimentally. The question of danger from gelatin made from treated hides has been raised and investigated. The consensus of opinion is that there is no danger from this source.

R. H. T.

Investigations on the Formation of Simple, Masked Chrome Complexes. III. Sulfatochromium Complexes in Pure Chromium Sulfate Solutions. By A. Küntzel, H. Erdmann and H. Spahrkäs. *Das Leder* **3,** 73 (1952). Previously it was pointed out that on titration of a sulfate-masked chrome liquor, the curve obtained by plotting volume of alkali against conductivity is not a straight line during precipitation of the chromium hydroxide but is curved (convex to the axis). This indicates that sulfate is present in two forms, one less stable than the other. Decomposition of the less stable complex results in a steeper first portion of the precipitation curve.

For the present experimental work the stock solution contained 7.6 per cent chromium (28.7% $Cr_2(SO_4)_3$) and had been aged at room temperature for 3 months after which its conducitivity was constant. For titration, the stock solution was diluted to N/3460. Titration curves at 25°C and 5°C were obtained by adding to 400 ml. of the dilute solution 2 ml. portions of N/200 sodium hydroxide at intervals of 0.5, 1, 2, or 5 minutes. Aging the diluted solution before titrating raised the curve and removed the curvature. Heating the stock solution to 40°, 60° or 100°, then diluting, aging, and titrating resulted in straight curves during precipitation but at high temperatures the initial precipitation point was lower. High temperatures favor formation of more stable complexes. The results in general indicate that in concentrated solutions at room temperature there are two kinds of coordinate compounds. One is stable on dilution whereas the other is more or less rapidly broken up. In the more stable complex a sulfato group forms a bridge between two chromium atoms. The less firmly bound sulfato group is attached to only one chromium atom and the complex is anionic. Other workers have noted that in concentrated chromium sulfate solutions or solutions that have been boiled, anionic complexes are present which change on dilution to cationic complexes with loss of sulfato groups. On the basis of the above work and of special, unpublished work by Erdmann on the conductivity of chromium sulfate solutions under different equilibrium conditions, the following three types of complexes are believed to exist; I, hexaquochromium sulfate (violet), $[Cr(OH_2)_6]^{+++}$ $(SO_4^{--})_3$; II, binuclear basic sulfato chromium sulfate, $[Cr_2(OH)_2(SO_4)]^{++}$ SO_4^{--}); III, binuclear, basic sulfato chromic acid, $[Cr_2(OH)_2(SO_4)_3]^{--}(H^+)_2$. There are equilibriums in solution between I and II, I and III, and II and III. Low concentrations favor formation of II and high concentrations, formation of III.

III has the following formula:



The formula of II is the same as that of III with the exception that the two SO_4 groups attached to Cr by single bonds leave the nucleus and are replaced by water (aq); the charge on the complex then changes from 2 negative to 2 positive. The loss of only one sulfato group does not give an uncharged complex but an amphoteric one which is especially favorable for union with amphoteric hide substance.

IV. The Influence of NaCl and Na_2SO_4 on the Basic Chrome Complex Existing in Chromium Sulfate Solutions. *Ibid.* **3,** 102. Technical chrome liquors, which are sulfate masked, may be treated with masking agents that are (1) weaker than sulfate, (2) equal to sulfate or (3) stronger than sulfate. The first two types will be considered here. The stock solution was a zero basic chromium sulfate solution containing one per cent chromium, free from neutral salts and aged for one year at room temperature. Portions of the stock solution were diluted to contain 0.1 per cent chromium after addition of 1, 2, or 4 equivalents of sodium chloride or sodium sulfate. On aging, there was a slight increase in conductivity for the first few hours then a very slow increase in solutions with no added salt or those with sodium chloride. The change was greater the greater the salt concentration. Conductivity increased, therefore there was a movement of complex bound sulfate out of the complex. Sulfate was not replaced by chloride because the latter does not form complexes as was shown in the first part of this study. Gustavson, from results with ion exchange resins, concluded that complex-bound chlorine was present in leather tanned with chromium chloride, in highly basic chromium chloride solutions, etc. This does not agree with the feeble complex activity of chloride ion and the fact that alkali tends to remove acid groups from the complex. The opposite effect, a slight decrease in conductivity, was found in solutions containing sodium sulfate. When the conductivity became constant, portions were diluted 200 fold and titrated with N/200 sodium hydroxide. As the sodium chloride content of the solutions increased, the curves were displaced more and more toward that of pure chromium chloride, and the curvature of the precipitation portion of the curve decreased. Sodium chloride changed the basic sulfato chromic acid (III) to basic sulfato chromium sulfate (II). The equilibrium displacement was caused by the presence of sodium ions which compete for the sulfate ions. The effect of sodium sulfate was the opposite of that of sodium chloride. The precipitation portion of the curve had greater curvature rather than less, and there was an increase instead of a decrease in anionic sulfato chromic acid.

V. Conductometric Measurements on the Reaction of Chromium Sulfate Solutions with Formate, Acetate and Oxalate. *Ibid.* **3,** 148. Conductivity changes on aging were measured in zero basic solutions of chromium sulfate and chromium chloride (0.1 per cent Cr) after addition of 0, 1, 2, 3, 4, or 6 equivalents, per atom of chromium, of sodium formate, acetate, or oxalate respectively. Without masking salt, conductivity of the sulfate was less than that of chloride because of the lower hydrogen ion concentration, the masking action of sulfate, and divalence of the sulfate ion. As masking salt was added, this difference of about 3 ordinate units decreased until with 6 equivalents the difference was only one ordinate unit. In the highly masked solutions the complex is the same and the conductivity difference is

due to the difference between sulfate and chloride ions. The conductivity drop on adding masking salt is much greater with chloride than sulfate. In each system the same number of organic groups enter the complex and lose their ionic character but in sulfate liquors, sulfate ions appear. Conductivity drops rapidly for 24 hours or less then slowly except for sulfate solutions containing not over 3 equivalents of masking salt. In this latter case there is a rise in conductivity because the mobility of formate and acetate ions is less than that of sulfate ions. With higher proportions of masking salt, conductivity drops because sulfate has all been displaced from the complex in the first phase. The rise in conductivity with oxalate has a different explanation because oxalate and sulfate ions have the same mobility. It is suggested that the divalent oxalate forms crosslinks and long-chain oxalate sulfato complexes which aggregate quickly then slowly deaggregate. The deaggregated complex with only one or two chromium atoms per nucleus, but of equal charge, has a much greater mobility than the highly aggregated complex ion. With increasing oxalate concentration this process loses meaning because the aggregation is overshadowed by the rapid formation of pure oxalato complexes.

Titration of aged, 0.1 per cent solutions, after dilution to N/3460, gave curves that were essentially the same whether masked with acetate, formate or oxalate. If 3 equivalents or more of masking salt were present, the curves for chromium chloride and for chromium sulfate were the same except for a trivial difference resulting from the fact that the mobility of sulfate idon is greater than that of the chloride ion. With less masking salt, it is not known whether there are mixed complexes or whether pure sulfato and pure oxalato complexes coexist. No information regarding amount of organic acid groups in the complex could be obtained by back titration with hydrochloric acid. In formate masked chromium sulfate solutions a maximum of 1.7 equivalents of formate per chromium atom were found in the complex, whereas 2 equivalents were found with chromium chloride. Chromium sulfate solutions could not be heated in sealed tubes to 100° without decomposition, but by careful heating to 70-90°, the formate content of the complex could be increased to 2 equivalents. With 6 equivalents of acetate in solution, 2.75 equivalents were obtained in the complex in one day and the amount did not increase on aging. However, the color of the solution changed showing that complex changes are possible that do not change conductivity. By heating in a sealed tube, 3 equivalents of acetate could be obtained in the complex but on aging there was a slow return to 2.75 equivalents. The complicated masking by acetate can probably be explained as follows: On addition of acetate the blue-violet triacetato complex forms at once. Unmasked highly basic chromium compounds probably are present also but do not influence color. The blue-violet color is the same as that of chrome solutions heated with 6 equivalents of acetate, and which were found to contain a triacetato complex. On aging for several months an equilibrium is established between the basic, unmasked chromium salts and the triacetato complex with formation of a basic acetato complex. This change does not alter the electrical charge on the complex because hydroxo and acetato radicals have the same charge, but there is a color change toward the green characteristic of the complex with 2 equivalents of acetate per chromium atom. The final equilibrium is toward the formation of the well known, green trichromium salt. If only 1 or 2 equivalents of acetate are added the final color is blue or red-violet without a green component. If 4 to 6 equivalents are added the green color of the trichromium salt (with 2 acetato groups in the complex) is changed toward blue-violet by the presence of triacetato complex. A previous report that only 2 acetato groups were found in the complex when 6 equivalents of acetate were added to chromium chloride, was an error. If sufficient oxalate was present, up to 3 mols of oxalate per chromium atom quantitatively entered the complex. The sodium salt of trioxalatochromic acid acted as a neutral, unbuffered salt and could be back titrated with hydrochloric acid. With 6 equivalents of oxalate in solution, 4 equivalents were found in the complex in 2 days and about 5 equivalents after further aging. On long aging the

green color is intensified. The solution may become turbid indicating a change from complexes of the trioxalato type to more highly aggregated, stable oxalatochromium compounds. I. D. C.

Prevention of Mold Growth on Shoes. By E. Belavsky and F. Pivovarov. *Calcados e Couros*, **21**, No. 215, 20 (1950). During the last world war it became important to prevent mold growth on shoes stored in warehouses in tropical and subtropical countries. Such growth depends upon the quantity of organic material originally in the leather and added in the manufacture of the shoes, such as adhesives, stains, dressings and finishes. The authors met this problem in Brazil. After considerable experimentation they advise all possible reduction of carbohydrate and proteins all along the line and consider it absolutely necessary to use fungicides during the production of both leather and shoes. They consider p-nitrophenol and mercuric chloride best for the purpose.

Requirements for the Production of a Fine Grain, Plump, Well Filled Chrome Upper Leather. By E. Belavsky and T. Termignoni. *Calcados e Couros*, **22**, No. 229, 22, No. 230, 22 (1951). Analyses show that vegetable tanned leather contains much more filling material, such as tannins, fats and other substances, than chrome tanned leather. As a result the vegetable tanned leathers are more compact and superior for military use. Typical comparative analyses are: Chrome tanned leather, hide substance 80 per cent, chromic oxide 3-8 per cent; vegetable tanned leather, hide substance 35 per cent, combined tannins 35 per cent, fats 30 per cent. The percentage of chromic oxide in the finished leather depends upon the following factors: concentration of the chrome liquor, basicity, tanning time, temperature of the chrome liquor and the effect of added salts (masking). The authors advise high concentration, basicity 33-60 per cent, tanning time not less than 8 hours and temperature at end of tanning not under 35 degrees C. The effect of adding sodium formate is much greater than for any other masking agent. For white leather it is better to add sodium acetate.

Advantages of the Modern Paste Drying System. By E. Belavsky and T. Termignoni. *Calcados e Couros*, **22**, No. 231, 18 (1951). Paste drying of chrome leathers must be done under more carefully regulated conditions than used in the usual drying method because, with the modern method, many operations are not needed, viz.: damping, staking and tacking or toggling. The leather, without these physical and mechanical operations, must become mellow, elastic and ready for finishing. Particular care must be taken in the last stage of drying, combining well controlled air conditioning with modern handling equipment. The authors recommend, in the last phase of drying, a rather low temperature and high relative humidity. It must be remembered that results obtained depend much upon the tanning and fatliquoring procedures. This new system gives the following advantages: much less working area required, more economical production, smoothness of grain surface, tight and elastic grain surface, better quality of flanks and some increase in area of leather made. Microphotographs and some detailed specifications are given.

Synthetic Resins as Ingredients of Leather and Shoe Finishes. By E. Belavsky and T. Termignoni. *Calcados e Couros*, **22**, No. 237, 20 (1952). The growth of the synthetic resin industry has brought about great changes in leather manufacture. The principal types of resins are: polymers of acrylic esters, polymers of vinyl esters and copolymers. For finishing leather it is best to use mixtures of different synthetic resins since they have

qualities which complement each other. Acrylic resins give a tough, tenacious, adhesive film not subject to roughening when stretched. The polyvinyl resins give a thicker film which covers better. Recently many copolymers have appeared on the market which give excellent results in combination with acrylic resins. Examples are: styrene-butadiene, acrylonitrile-butadiene, and vinilydene chloride-acrylonitrile. Polychloropropene is also a good ingredient. The authors give a classification of the resins currently available. Ten advantages of using synthetic resins for finishing leather are: finishing better and cheaper, film is thermoplastic and will therefore bind more pigment without producing a painted or superimposed film appearance, more blemishes are covered increasing the value of the leather, much less work without glazing, the finish flows when hot pressed giving better binding and smoother grain, finishes do not ferment, greater water resistance, the tough elastic binder and pigment will produce a synthetic grain surface on split leather which approaches the properties of a true grain leather, finish does not crack or peel when lasting during the manufacture of shoes, repairing of shoes during fabrication is easy and satisfactory.

Application of Scientific Methods to Shoe Manufacture. I. Lasting. By E. Belavsky. *Calcados e Couros*, **22,** No. 235, 18 (1952). The effect of the relative humidity of the atmosphere upon the water content, strength and stretch, and area change of chrome tanned calf leather as well as the strength and stretch of various satisfactory leathers is demonstrated. The advantages of modern mulling methods in a cabinet or tunnel equipped with a humidifying device, which supplies moisture in the form of a very fine vapor, are indicated.

Application of Scientific Methods to Shoe Manufacture. II. Dressing. By E. Belavsky. *Calcados e Couros*, **22,** No. 236, 22 (1952). The uppers must be well prepared for dressing. Upon cleaning and ironing depends much of the finished beauty of the shoes. Pigment finished leathers are exceptionally susceptible to the action of harsh cleaners. Too much alcohol or too strong ammonia wash have the tendency to open up the grain giving it a harsh, rough scaly feel and appearance. It is best to use a weak solution of a neutral soap or sulfonated oil. Too much heat destroys the appearance and character of the upper leather. Temperature should be regulated by modern rheostat control. Up to the present, finishes have usually been made of a shellac base solubilized by alkali. This method has various disadvantages. There is a tendency for the finishes to "break" on the vamp while in stock or in show windows. Even a good solid leather may show a "pipy" grain in the finished shoe. The author recommends the use of modern polishes made from waxes or synthetic resins.

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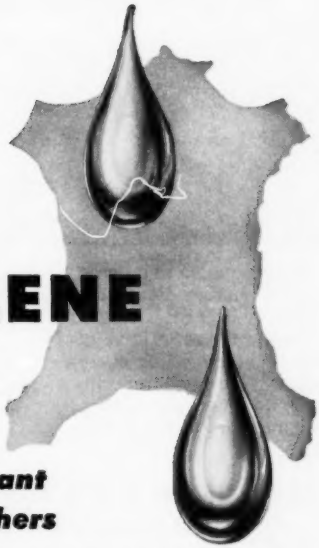

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